

Advances in

**ORGANOMETALLIC
CHEMISTRY**

VOLUME 19

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Advances in Organometallic Chemistry

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Chemistry of Titanocene and Zirconocene

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I

INTRODUCTION

Bis(η -cyclopentadienyl)titanium or titanocene, $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ (1), and bis(η -cyclopentadienyl)zirconium or zirconocene, $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}$ (2), although frequently referred to in the literature, have never actually been isolated as discrete chemical compounds. However, these molecules have been implicated as highly reactive intermediates in a wide variety of chemical reactions with olefins, hydrogen, carbon monoxide, and dinitrogen. In recent years some discrete, well-characterized bis(η -cyclopentadienyl) and bis(η -pentamethylcyclopentadienyl) complexes of low-valent titanium and zirconium have been isolated and studied, and it has become possible to understand some of the reasons for the remarkable reactivity of titanocene- and zirconocene-related organometallics toward small unsaturated molecules.

In this chapter we will review the synthesis, structural aspects, and basic chemical properties of formally divalent and trivalent titanium and zirconium metallocene complexes. We have restricted our coverage to the low-valent bis(η -cyclopentadienyl) and related metallocenes; metal halide complexes and organometallic mixed metal systems will not be discussed here. We have not attempted to present an exhaustive coverage of the field. Rather, our aim has been to describe critically and to evaluate the often confusing chemistry that has been reported for the reactive low-valent titanium and zirconium metallocenes. More general reviews (1) and a book (2) on the organometallic chemistry of titanium, zirconium, and hafnium have been published.

A. Experimental Aspects

The synthesis and handling of low-valent titanium and zirconium metallocenes require special experimental procedures because of the extreme sensitivity of the compounds toward oxygen, moisture, and sometimes even dinitrogen. Schlenk-type glassware, commonly used for handling air-sensitive materials, does not generally afford sufficient protection. For our work we have used a Vacuum Atmospheres (Vacuum Atmospheres Corp., Los Angeles, Cal.) argon filled drybox with <5 ppm O_2 or moisture for the transfer and manipulation of solids. The drybox is kept free of solvents; all (volatile) solvents and reactant gases are transferred on high-vacuum lines.

Not only are the metallocenes very sensitive to normal ambient conditions but, because of the great strength of the $\text{Ti}-\text{O}$ and $\text{Zr}-\text{O}$ bonds, the compounds are often irreversibly decomposed by polar organic com-

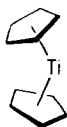
pounds (e.g., aldehydes, ketones, alcohols). However, the metallocenes can as a general rule be handled in hydrocarbon and in ether solvents. For similar reasons, the compounds react irreversibly with most of the polar solids (e.g., silica, alumina, etc.) that are commonly used for liquid chromatography. Thus, methods of purification are mostly limited to solvent extraction, sublimation, and recrystallization techniques. Experimentally, the most challenging task is the isolation of single crystals (for characterization and X-ray structural work) of the highly reactive complexes. Methods used successfully for growing single crystals are the two-layer solvent diffusion technique and the slow-evaporation method; these are described in the experimental sections of references (3) and (4), respectively.

B. Theoretical Background

Elements of the first transition series from vanadium to nickel form stable bis(η -cyclopentadienyl) complexes having the normal π -sandwich structure typical of ferrocene. In contrast, bis(η -cyclopentadienyl)titanium, (η -C₅H₅)₂Ti (1), is not even known as a discrete compound.

In 1963, Vol'pin *et al.* (5) suggested that transition metal complexes having a particular electronic configuration [i.e., possessing at least (a) one available electron pair and (b) one unfilled orbital in the valence shell] should possess chemical characteristics akin to those of carbenes. By the above criteria, (η -C₅H₅)₂Ti (1) was considered to be such a "carbenoid," and it was expected that it should undergo facile bond addition and bond insertion reactions, by analogy with the chemistry of carbenes. As an experimental support for this hypothesis, it was shown that a nascent (C₅H₅)₂Ti (assumed to form in the reaction of TiCl₄ and Na⁺C₅H₅⁻) reacted with diphenylacetylene to yield what is now known as the metallocycle (η -C₅H₅)₂Ti(C₆H₅C₂C₆H₅)₂ (Section V,A,2).

Brintzinger and Bartell (6) later reported results of extended Hückel calculations that seem to support these intuitive ideas of Vol'pin and his associates. Calculations of the variation in the total energy of (η -C₅H₅)₂Ti with respect to ω , the angle between the planes of the C₅H₅ rings, indicate that titanocene (1) is most stable in the bent configuration with $\omega = 30$ –40°.



(1)

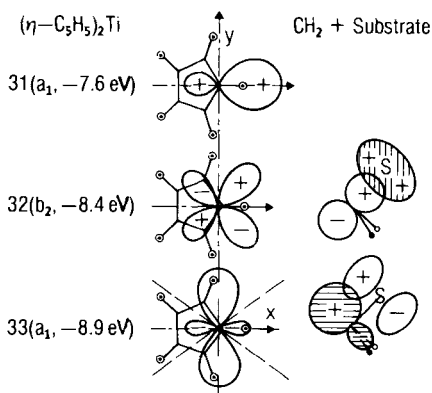


FIG. 1. Schematic representation of the essentially nonbonding molecular orbitals in a bent $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ molecule ($\omega = 30^\circ$). For comparison, the corresponding orbitals of a carbene and their interactions with bonding and antibonding orbitals are traced at the right (hatched orbitals are doubly occupied). Reprinted with permission from Brintzinger and Bartell (6), *J. Am. Chem. Soc.* **92**, 1106 (1970). Copyright 1970 by the American Chemical Society.

Vanadocene, $(\eta\text{-C}_5\text{H}_5)_2\text{V}$, on the other hand is most stable with $\omega = 0^\circ$, i.e., in the normal π -sandwich configuration with the cyclopentadienyl rings parallel. This may be part of the reason that $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ -related species show a much richer chemistry with H_2 , N_2 , or olefin substrates than vanadocene. The analogy between $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ (1) and a carbene has been illustrated, from a molecular orbital point of view, in Fig. 1. In the interaction of a bent $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ (1) with a substrate, the two lower lying orbitals, $33(a_1)$ and $32(b_2)$, are considered to perform similar roles to the σ and π orbitals, respectively, of a singlet R_2C carbene. Appropriate addition and insertion reactions with a substrate can thus take place. Brintzinger, Lohr, and Wong (6) and also Lauher and Hoffman (7) have subsequently discussed in more detail the electronic configuration, structure, and chemistry of "bent" $(\eta\text{-C}_5\text{H}_5)_2\text{M}$ and $(\eta\text{-C}_5\text{H}_5)_2\text{M-L}_n$ complexes.

II

SYNTHESIS OF LOW-VALENT TITANIUM AND ZIRCONIUM METALLOCENES

A. Synthesis of Bis(η -cyclopentadienyl)titanium Complexes

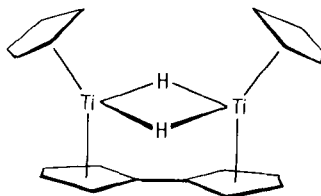
1. Attempts at the Preparation of Titanocene $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ (1)

In 1956, following the synthesis of ferrocene by Kealy and Pauson (8), Fischer and Wilkinson (9) reported the isolation of a dark green, diamag-

netic, air-sensitive solid from the reaction of titanium dichloride with cyclopentadienyl sodium. The green solid was thought to be titanocene ($(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ (1). Watt and Baye (10) later tried to duplicate this synthesis but were unable to obtain any product of composition $(\text{C}_5\text{H}_5)_2\text{Ti}$, and they therefore expressed considerable doubt about the existence of titanocene. Subsequent workers tried to prepare titanocene (1) by the thermal decomposition (11–14) or hydrogenolysis (Section II,A,3) of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ and $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$. These reactions yielded dark solids which, in many cases, have not been adequately characterized (2). Several attempts were made to prepare titanocene by de-halogenation of bis(η -cyclopentadienyl)titanium dichloride. Reaction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with sodium amalgam in toluene (15), or with sodium naphthalene in tetrahydrofuran (16), was reported to yield green, air-sensitive products. These were assigned the composition $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$ and $(\text{C}_5\text{H}_5)_2\text{Ti}$, respectively, on the basis of elemental analyses, molecular weight measurements, and infrared spectra. A related "titanocene" material, obtained by reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with sodium, was considered on the basis of its infrared spectrum not to be a simple π -sandwich complex, i.e., $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ (1), but a more complex, mixed σ - and π -bonded cyclopentadienyl titanium compound (17).

2. Preparation of $\mu\text{-(}\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8\text{)-}\mu\text{(H)}_2\text{-(}\eta\text{-C}_5\text{H}_5\text{)}_2\text{Ti}_2$ (3)

Brintzinger and Bercaw (18) clarified the identity of these various "titanocene" solids. They found that the light green material, which is the main product in the various reactions of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with Na, Na/Hg, and sodium naphthalene, is in fact a complex, dimeric metal hydride of composition $[(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)\text{TiH}]_2$ (3). The compound is characterized by an intense metal-hydride stretching frequency which appears at 1230 cm^{-1} . The detailed structure of 3 was later established (18a) from ^{13}C -NMR studies as $\mu\text{-(}\eta^5\text{:}\eta^5\text{-fulvalene)-}\mu\text{-dihydridobis(}\eta\text{-dicyclopentadienyltitanium), } \mu\text{-(}\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8\text{)-}\mu\text{(H)}_2\text{-(}\eta\text{-C}_5\text{H}_5\text{)}_2\text{Ti}_2$ (3)



(3)

Crystals of 3 apparently proved to be unsuitable for X-ray structural work; however, the molecular geometry of 3 as illustrated was confirmed



FIG. 2. Postulated rearrangement of bis(η⁵-cyclopentadienyl)titanium to (η⁵-cyclopentadienyl)(η¹-cyclopentadienyl)titanium hydride. Reprinted with permission from Brintzinger and Bercaw (18), *J. Am. Chem. Soc.* **92**, 6184 (1970). Copyright 1970 by the American Chemical Society.

by an X-ray structural determination of the bis-hydroxy derivative μ -(η⁵:η⁵-C₁₀H₈)-μ(OH)₂-(η-C₅H₅)₂Ti₂ (19).

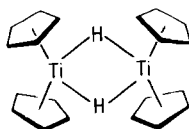
The formation of hydride **3** in various (η-C₅H₅)₂TiCl₂ or (η-C₅H₅)₂Ti(CH₃)₂ reduction reactions has been reasonably explained (18) by assuming the formation of a (η-C₅H₅)₂Ti "carbenoid" intermediate in these reactions. Carbenes are known to rearrange by an α-hydrogen abstraction process to yield an olefin. By analogy, the highly coordinatively unsaturated titanium(II) center in the bent (η-C₅H₅)₂Ti intermediate could abstract hydrogen from the C₅H₅ ligand to yield a titanafulvene-hydride structure (Fig. 2). This could then dimerize to yield **3**.

The hydride (**3**) can be conveniently prepared by reaction of (η-C₅H₅)₂TiCl₂ (1 mol) with sodium naphthalene (2 mol) in tetrahydrofuran at room temperature. This is essentially the technique described by Watt and Drummond (16) for the preparation of "titanocene." The solid remaining after removal of naphthalene and THF in vacuo is extracted with benzene. The light green hydride obtained by evaporation of the benzene extracts can be purified by washing with a little benzene (in which it is only sparingly soluble). Traces of any (C₅H₄)(C₅H₅)₃Ti₂ (Section II,A,4) can be removed by treatment with 1-pentene (20). Infrared spectra of **3** in Nujol display an intense ν_{M-H} band at 1230 cm⁻¹. The complex is extremely air-sensitive. Slight oxidation (e.g., by brief exposure of the Nujol oil mull to air) results in a total loss of the 1230 cm⁻¹ band. This may explain why the intense 1230 cm⁻¹ absorption was not observed by Watt and Drummond (see comment as Note Added in Proof in reference 18). It is very likely that most of the "titanocene" materials referred to in the literature prior to 1971 consist mainly of this hydride complex **3**.

3. Synthesis of Dinitrogen-Reactive "Titanocenes"

The discovery in 1964 by Vol'pin and Shur (47) of N₂ reduction by (η-C₅H₅)₂TiCl₂/RMgX mixtures (Section III,A) led several workers to postulate the intermediacy of (η-C₅H₅)₂Ti in these dinitrogen fixation systems.

The chemical properties of hydride complex **3** (once thought to be titanocene) are unexceptional; certainly it does not react with N_2 under reasonable conditions (10 atm, 23°C). The possibility that a "real" titanocene, i.e., $(\eta-C_5H_5)_2Ti$ (**1**), might indeed bind dinitrogen stimulated a great deal of effort to synthesize it. With this objective in mind, Brintzinger and co-workers carefully studied the reaction of bis(η -cyclopentadienyl)dimethyltitanium with hydrogen, which had also previously been reported to yield "titanocene" (**21**) (Section II,A,1). They found that, whereas hydrogenolysis of $(\eta-C_5H_5)_2Ti(CH_3)_2$ (**4**) solutions at room temperature yields mainly hydride **3**, reaction of solid $(\eta-C_5H_5)_2Ti(CH_3)_2$ (**4**) with hydrogen yields a purple complex reasonably characterized as the bridging hydride (**5**).



(5)

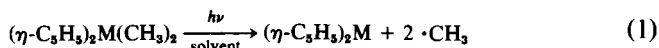
The antisymmetric ν_{Ti-H} vibration for this compound is seen as an intense broad absorption at 1450 cm^{-1} (**22**). In contrast, treatment of a saturated hexane solution of $(\eta-C_5H_5)_2Ti(CH_3)_2$ (**4**) with H_2 at 0°C gave a gray-green, presumably polymeric hydride, $[(C_5H_5)_2TiH]_x$ (**6**), having a characteristic ν_{Ti-H} absorption at 1140 cm^{-1} (**23**, **24**).

A slurry of this hydride in toluene slowly decomposed giving H_2 and a dark, slightly green solution that was claimed to contain the titanocene dimer $[(C_5H_5)_2Ti]_2$ (**7**). The latter was described as a "metastable titanocene," since upon heating to 100°C it decomposed to the fulvalene hydride complex **3**. This dimer (**7**) and its parent hydride (**6**) were formulated as $[(C_5H_5)_2Ti]_2$ and $[(C_5H_5)_2TiH]_x$, respectively, on the basis of quantitative chemical reactivity studies with HCl, DCl, and carbon monoxide; by their infrared spectra; and (for **7**) by molecular weight measurements (**23**, **24**). However, adequate criteria to establish the purity and therefore the exact compositions of **6** and **7** were not presented. The compounds were not obtained as crystalline solids; elemental analyses that could substantiate the stated composition as $[(C_5H_5)_2TiH]_x$ (**6**) and $[(C_5H_5)_2Ti]_2$ (**7**) were not reported. The infrared spectrum of **7** was said to show absorptions typical of metallocene compounds; this was cited as an indication that in **7** there are only "simple," i.e., $(\eta-C_5H_5)$, ligands. However, subsequent work with crystalline $\mu-(\eta^1:\eta^5-C_5H_4)(\eta-C_5H_5)_3Ti_2C_4H_8O \cdot C_4H_8O$ (Section II,A,4) has shown that infrared spectra are not necessarily indicative of the presence of only $(\eta-C_5H_5)$, cyclopentadienyl ligands. We believe that

considerable further work is needed to determine the exact composition of hydride **6** and also to demonstrate convincingly that **7** is indeed the dimeric titanocene $[(C_5H_5)_2Ti]_2$. This "metastable titanocene" **7**, in contrast to hydride **3**, readily reacts with N_2 to give a deep blue complex, claimed to have the composition $[(C_5H_5)_2Ti]_2N_2$ (23, 24). The identity, preparation, and properties of this complex and of other titanocene-based dinitrogen complexes will be discussed in Section III.

Other attempts have been made at preparing dinitrogen reactive "titanocenes." Van Tamelen and co-workers (25) monitored the successive reaction steps in the reduction of $(\eta-C_5H_5)_2TiCl_2$ with excess sodium in toluene, using visible and infrared spectra. The reaction was said to give successively $[(\eta-C_5H_5)_2TiCl]_2$, $[(\eta-C_5H_5)_2Ti]_{1-2}$ (**8**), $[(\eta-C_5H_5)-(C_5H_4)TiH]_x$, and finally the hydride $[(\eta-C_5H_5)(C_5H_4)TiH]_2$ (most likely **3**). The second complex, $[(\eta-C_5H_5)_2Ti]_{1-2}$ (**8**), was referred to as a "highly unstable," "active titanocene." It was found to react with dinitrogen to give a deep blue complex. The composition of **8** was inferred only on the basis of an infrared spectrum and on its reactivity with CO to yield $(\eta-C_5H_5)_2Ti(CO)_2$. Basic data, such as elemental composition, criteria of purity, and other characterization reactions supporting the formula $[(\eta-C_5H_5)_2Ti]_{1-2}$ (**8**), were not presented in the brief communication (25). No other reports on this work have since appeared. There is still considerable uncertainty as to the stated identity of this so-called "active titanocene."

Alt and Rausch (26) have claimed that low-valent titanium, zirconium, and hafnium metallocenes can be prepared by photolysis of the corresponding bis(η -cyclopentadienyl)metal dimethyl complexes



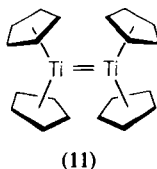
By this method, a so-called black titanocene (**9**) was obtained. This material analyzed for the empirical elemental composition $C_{10}H_{10}Ti$ (26) or $C_{10}H_{9-10}Ti$ (27). It was found to be diamagnetic, less volatile than **3**, and reported to react with CO to give $(\eta-C_5H_5)_2Ti(CO)_2$ (in 60% isolated yield) and with dinitrogen in tetrahydrofuran to give a purple complex. It was not adequately demonstrated that this "black titanocene" is indeed a single compound, and its molecular structure and relationship to the various other dinitrogen-reactive "titanocenes" are not at all clear.

Rausch and co-workers (28) have more recently reported that photolysis of bis(η -cyclopentadienyl)diphenyltitanium, $(\eta-C_5H_5)_2Ti(C_6H_5)_2$, also gives a "black titanocene" **9a**. The latter is similar, but not identical in all its properties, to **9**. On the other hand, Brubaker *et al.* (29) have found that irradiation of $(\eta-C_5H_5)_2Ti(C_6H_5)_2$ gives the hydride $[(C_5H_5)_2TiH]_x$ as a final product. The latter is claimed to be similar in its

properties to the gray-green hydride complex **6** reported by Brintzinger *et al.* Brubaker *et al.* have postulated that various solvated $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ complexes are formed as reaction intermediates in the photolytic decomposition of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5)_2$. In the presence of CO and diphenylacetylene, the stable derivatives $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ and $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_6\text{H}_5\text{C}_2\text{C}_6\text{H}_5)_2$ (Section V,A,2) were obtained (29). However, the proposed $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{solvent})$ intermediate titanocene species were neither isolated nor unambiguously identified.

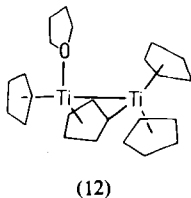
4. Preparation of $\mu\text{-(}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{)}(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**)

As pointed out earlier, the elusive nature of titanocene is consistent with its formulation as a carbene-like species (Section I,B). It is difficult to imagine that such a carbenoid could exist as an isolated, stable entity. However, we felt that its metal-metal bonded dimer, the "metallic olefin" species **11**,



might perhaps be prepared as a stable compound, by the dimerization of an $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ intermediate, provided that low temperatures were used to avoid rearrangements to complex hydrides such as **3**. [Certain electron-rich carbenes are known to exist in equilibrium with olefin dimers (30).]

In fact, reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ (1 mol) with potassium naphthalene (2 mol) at -80°C followed by slow warming to room temperature and suitable work-up afforded a gray-black powder, subsequently characterized as $\mu\text{-(}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{)}(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**) (3). A crystalline derivative was obtained by slow diffusion of isopentane into solutions of **10** in tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$). An X-ray structural investigation gave the composition of this tetrahydrofuran derivative as $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)\text{Ti}(\eta\text{-C}_5\text{H}_5)(\text{C}_4\text{H}_8\text{O})\cdot\text{C}_4\text{H}_8\text{O}$ (**12**).



Molecule **12** consists of three ($\eta\text{-C}_5\text{H}_5$) cyclopentadienyl ligands and one bridging ($\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4$) cyclopentadienyl ligand arranged around a Ti–Ti framework. One molecule of tetrahydrofuran is bonded to the formally divalent titanium atom; the second molecule of tetrahydrofuran occupies a diffuse position in the cell. The composition of **12** as $\text{C}_{20}\text{H}_{19}\text{Ti}_2(\text{C}_4\text{H}_8\text{O})\cdot\text{C}_4\text{H}_8\text{O}$, i.e., containing one hydrogen atom less in a cyclopentadienyl ligand than in a titanocene dimer $\text{C}_{20}\text{H}_{20}\text{Ti}_2$, was unexpected. We could find no chemical or crystallographic evidence for the presence of a hydride atom in **12** although it is difficult to rule out completely the possibility of the presence of such a hydride atom.

The tetrahydrofuran adduct molecules in **12** can be removed by dissolving the complex in octane and evaporating the solution in vacuo. This affords a method of preparing very pure samples of $\mu\text{-(}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{)}(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**). It was not possible to prepare single crystals of **10**. We believe that the latter has essentially the same framework structure as its bis-tetrahydrofuran adduct **12**. Support for this view comes from the molecular structure of a dinitrogen derivative of **10** wherein an N_2 ligand atom occupies the formally divalent titanium, tetrahydrofuran coordination site of **12** (Section III,D).

A model of **10** (which is essentially **12** less the tetrahydrofuran ligands) shows a large degree of openness or structural unsaturation on the one side of the Ti–Ti linkage that is not bridged by the ($\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4$) ligand. There is a geometrically exposed and coordinatively unsaturated titanium–titanium bond, reminiscent of an “edge” in a metallic crystal. This structural unsaturation, combined with the high degree of electron unsaturation in the molecule, accounts for much of its striking chemical behavior with N_2 , H_2 , and olefins (**3**, **20**) (Sections III,D and VI, respectively).

5. Summary: A Comparison of the Various “Titanocenes”

The reader might at this point question the relationships between the various low-valent titanium metallocene complexes that have been described. Unfortunately, at the present stage of development of the field, only partial answers can be given.

Thus far, only two “titanocene” complexes have been reasonably well characterized. These are the fulvalene-bridged bis(η -cyclopentadienyl-titanium)dihydride, $\mu\text{-(}\eta^5\text{-C}_{10}\text{H}_8\text{)-}\mu\text{(H)}_2\text{-(}\eta\text{-C}_5\text{H}_5\text{)}_2\text{Ti}_2$ (**3**), and the bridging ($\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4$ -cyclopentadienyl)tris(η -cyclopentadienyl)ditanium(Ti–Ti) complex, $\mu\text{-(}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{)}(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**). Hydride **3** (a light green, very air-sensitive solid) is the most stable of the various “ti-

tanocenes," and it seems to be at least the major product in the uncontrolled reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ and $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ complexes (Sections II,A,1,2 and 3).

There is at least a superficial resemblance in the properties of $\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**) (3) and the compound formulated as $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$ (**7**) by Brintzinger and co-workers (24). The infrared spectra and the chemical reactivity of the two compounds with hydrogen are very similar. Reaction of **10** with H_2 reversibly yields a gray-green hydride of composition $(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)_3\text{Ti}_2\text{H}_2$ [or $(\text{C}_5\text{H}_5)_4\text{Ti}_2\text{H}$] (**20**)—which has the same appearance and infrared spectrum ($\nu_{\text{TiH}} = 1140\text{ cm}^{-1}$) as $[(\text{C}_5\text{H}_5)_2\text{TiH}]_x$ (**6**), the precursor to $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$ (**7**). Compounds **10** and **7** react with N_2 under similar conditions to give deep blue, but apparently different dinitrogen complexes. The stoichiometry of N_2 absorption suggests the compositions $[(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)_3\text{Ti}_2]_2\text{N}_2$ (**20**) and $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ (**24**), respectively, for these complexes (Sections III,C and D). Finally, both **10** and **7** form adducts when treated with tetrahydrofuran. However, solutions of **10** in tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$) appear to be more stable than those of **7**, and have been utilized for the preparation of the crystalline bis-tetrahydrofuran derivative of **10**, i.e., $\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2(\text{C}_4\text{H}_8\text{O})\cdot\text{C}_4\text{H}_8\text{O}$ (**12**).

The "highly unstable," "active titanocene" **8**, reported by van Tamele *et al.*, also forms a blue complex with dinitrogen, $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ (**25**) (Section III,C). Interestingly, the visible absorption spectrum of this "titanocene" **8** is identical with that of $\mu\text{-}(\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**) (bands at 486 and 640 nm) (3). Unfortunately however for comparative purposes, the reported spectrum of **8** does not cover the near infrared region at $\sim 1120\text{ nm}$ where **10** shows a characteristic intervalence absorption band.

The "black titanocenes" **9** and **9a**, $\text{C}_{10}\text{H}_{10}\text{Ti}$ (**26**) or $\text{C}_{10}\text{H}_{9-10}\text{Ti}$ (**27**), reported by Rausch *et al.* appear to be quite different from the compounds described above. For instance, **9** is diamagnetic and has a different absorption spectrum (bands at 700 and 826 nm) from that of **10**. Note however, that hydride **3** has a strong absorption band at 824 nm (3). Unlike **10** and $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$ (**7**), black titanocene (**9**) does not appreciably decompose to hydride **3** on prolonged heating of solutions in toluene. Solutions of **9** in tetrahydrofuran are said to react with dinitrogen to give a purple, but otherwise unidentified, dinitrogen complex. No mention is made of the formation of any blue dinitrogen complexes in toluene, a characteristic property of **7**, **8**, and **10**. Note, however, that **10** forms a red-brown dinitrogen derivative in tetrahydrofuran (Section III,D). Rausch and co-workers (27) now believe **9** to be an oligomeric titanium metallocene containing C_5H_5 and C_5H_4 ligands. The other black titanocene (**9a**) is said to be similar to **9** except that it is not pyrophoric in air (28). Some further contrasts in the

chemistry of these "titanocenes" have been gleaned from the reactivity of the compounds with ammonia (Section IV).

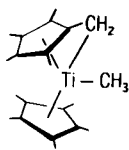
It is unfortunate that many of these low-valent titanium metallocenes have simply been referred to in the literature as one form or another of titanocene. Compositions **7**, **8**, **9**, and **9a** have not been adequately identified, and it seems unlikely that any of these are $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ or $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2$.

B. Synthesis of Bis(η -pentamethylcyclopentadienyl)titanium and Zirconium Complexes

The possible rearrangement of intermediate $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$, "carbenoid" species by a transfer of hydrogen from the ligand to give complex metal hydrides (i.e., **3**) has been referred to above (Sections I,B and II,A,2). In attempts to prepare N_2 -reactive low-valent titanium metallocenes, Bercaw and Brintzinger (31) sought to minimize the possibility of this hydrogen transfer reaction by using pentamethylcyclopentadienyl, $[\eta\text{-C}_5(\text{CH}_3)_5]$, instead of $(\eta\text{-C}_5\text{H}_5)$ ligands. They hoped to obtain the highly coordinatively unsaturated bis(η -pentamethylcyclopentadienyl)titanium or permethyltitanocene, $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Ti}$.

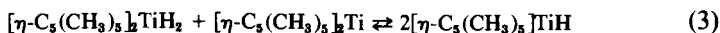
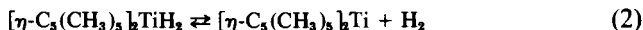
1. Preparation and Basic Chemical Properties of Permethyltitanocene (24, 32)

Several possible routes to the preparation of $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Ti}$ were explored. First attempts at the dehalogenation of $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{TiCl}_2$ gave uncharacterizable oily products. Another synthetic method involving the dealkylation of $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Ti}(\text{CH}_3)_2$ (**13**) proved to be quite difficult. The dimethyltitanium complex **13** was found to be very stable, in contrast to $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ (**4**) which decomposes at room temperature. The permethylated complex **13** was even unaffected by hydrogen (100 atm) at 25°C. However, upon heating solutions of **13**, a turquoise compound of composition $[\text{C}_5(\text{CH}_3)_5][\text{C}_5(\text{CH}_3)_4\text{CH}_2]\text{TiCH}_3$ (**14**) was formed, concurrent with the evolution of methane. The composition and structure for **14** were proposed on the basis of the stoichiometry of its formation and on NMR, infrared, and mass spectral data.



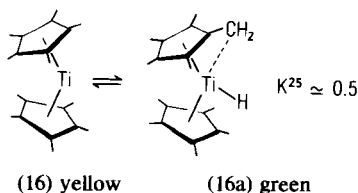
(14)

Reaction of **14** with H_2 in pentane gave, on cooling, orange crystals of the hydride $[\eta-C_5(CH_3)_5]_2TiH_2$ (**15**). Dissolution of **15** in pentane, under vacuum, was originally reported to yield permethyltitanocene, $[\eta-C_5(CH_3)_5]_2Ti$ (**16**), in equilibrium with a dimer, $[(\eta-C_5[CH_3]_5)_2Ti]_2$ (**17**) (24). However, in a later, more detailed examination of this reaction, it was shown (32) that when $[\eta-C_5(CH_3)_5]_2TiH_2$ (**15**) is dissolved in pentane in vacuo, it slowly loses hydrogen in a stepwise sequence involving the two equilibria:



A mixture of permethyltitanocene, $[\eta-C_5(CH_3)_5]_2Ti$ (**16**), and the monohydride complex, $[\eta-C_5(CH_3)_5]_2TiH$ (**18**), is obtained. The earlier report (24) relating to the formation of the dimer, $[(\eta-C_5[CH_3]_5)_2Ti]_2$ (**17**), proved to be incorrect. In fact, all the bis(η -pentamethylcyclopentadienyl)titanium species studied appear to be monomeric. This is in contrast to the chemistry of bis(η -cyclopentadienyl)titanium systems wherein most compounds, for example **3** and **10**, are dimeric.

The best method for preparing pure permethyltitanocene (**16**) is via a dinitrogen adduct. Addition of N_2 to a solution of partially dehydrogenated $[\eta-C_5(CH_3)_5]_2TiH_2$ (**15**) in toluene yields the dinitrogen complex, $[(\eta-C_5[CH_3]_5)Ti]_2N_2$ (**19**), which was isolated as a blue-black microcrystalline precipitate by cooling the solution to $0^\circ C$ (Section III,E). At room temperature and in vacuo, solutions of this complex slowly release dinitrogen. Complete removal of solvent yields permethyltitanocene (**16**) as a yellow-orange crystalline solid. Solutions of permethyltitanocene (**16**) are slowly transformed, at room temperature, into a yellow-green, equilibrium mixture of $[\eta-C_5(CH_3)_5]_2Ti$ (**16**) and its tautomer $[C_5(CH_3)_5]^- [C_5(CH_3)_4CH_2]^+ TiH$ (**16a**):



It is interesting that the $[C_5(CH_3)_5]_2Ti$, 14-electron metallocene "carbenoid" even inserts into the hydrocarbon-like C—H bond of a pentamethylcyclopentadienyl ligand. Significantly, however, the reaction is reversible, whereas with bis(η -cyclopentadienyl) systems the formation of complex hydrides (Sections II,A,1 and 2) seems to be an irreversible pro-

cess. The existence of the above tautomeric equilibrium apparently does not seriously restrict stoichiometric utilization of $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Ti}$ (**16**) as, for example, in reactions with N_2 (Section III,E). Although it is sufficiently stable for characterization and chemical reactivity studies, permethyltitanocene decomposes irreversibly upon prolonged storage at room temperature to give a violet paramagnetic complex $[\text{C}_5(\text{CH}_3)_5]\text{-}[\text{C}_5(\text{CH}_3)_4\text{CH}_2]\text{Ti}$ (**21**).



2. Concerning *Bis*(η -pentamethylcyclopentadienyl)zirconium

The *bis*(η -pentamethylcyclopentadienyl)zirconium dinitrogen complex $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Zr}_2(\text{N}_2)_3$ (**22**), in solution reversibly releases its dinitrogen in vacuo over several hours (Section III,E). The solutions remaining are said to consist mainly of $[\eta\text{-C}_5(\text{CH}_3)_5][\eta\text{-C}_5(\text{CH}_3)_4\text{CH}_2]\text{ZrH}$ (**23**) (**33**). Permethylzirconocene $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Zr}$ (**24**) may exist in these solutions in equilibrium with this hydride tautomer (as in the case of titanium). However, thus far permethylzirconocene has not been isolated as a discrete compound or otherwise characterized. It is very likely that permethylzirconocene is less stable and more prone to form complex metallocene hydrides than permethyltitanocene (**16**).

C. Concerning *Bis*(η -cyclopentadienyl)zirconium

Bis(η -cyclopentadienyl)zirconium or zirconocene, $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}$ (**2**), has been referred to in the literature (26, 34–36), but in fact a compound of this formula has actually never been isolated or in any way identified. It appears that $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}$ and related intermediate species tend more readily to form complex hydrides than those of titanium. One reason for this may be the greater strength of the Zr-H versus the Ti-H bond, as illustrated by the heats of formation of the dihydrides: $\text{TiH}_{1.971}$, $\Delta H_{f,298}^\circ = -29.5$ kcal/mol; ZrH_2 , $\Delta H_{f,298}^\circ = -38.9$ kcal/mol (37). Another factor may be the generally higher strength of the zirconium-carbon versus the titanium-carbon bond (38). Trivalent titanium forms “normal” $(\eta\text{-C}_5\text{H}_5)$ metallocene halide complexes, whereas even zirconium(III) can

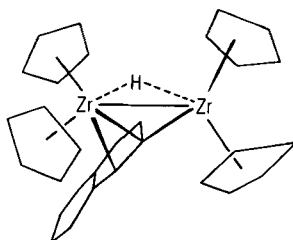
form a complex, metallocene ring system as presumably exists in $C_{10}H_8ZrCl$ (39).

1. Attempts at the Preparation of Zirconocene

The major reference in the literature is due to Watt and Drummond (34) who reported that $(C_5H_5)_2Zr$ could be prepared as a purple-black solid by reaction of $(\eta-C_5H_5)_2ZrCl_2$ with sodium naphthalene in tetrahydrofuran. The formula $(C_5H_5)_2Zr$ was assigned on the basis of elemental analyses and an infrared spectrum (35), which showed no apparent metal hydride absorptions. However, in view of the complex hydride structure found for the literature "titanocene" (compound 3, Sections II,A,1 and 2), it was suspected that this "zirconocene" might likewise be a very complex metallocene metal hydride. Reduction of $(\eta-C_5H_5)_2ZrCl_2$ with potassium naphthalene, under rigorously anaerobic conditions, gave a purple solid having an intense broad metal hydride band in the infrared at 1200–1500 cm^{-1} . Brief exposure of the Nujol oil mull to air resulted in a total loss of this absorption, and the resulting infrared spectrum was found to be very similar to that reported by Watt and Drummond (35) for the purple solid "zirconocene." This $(C_5H_5)_2Zr$ is thus certainly a zirconium hydride with complex cyclopentadienyl (C_5H_4) or fulvalenyl ($C_{10}H_8$) ligands (4). The preparation of a dark brown zirconocene (and a gray hafnocene) by photolysis of $(\eta-C_5H_5)_2M(CH_3)_2$ ($M = Zr, Hf$) has been claimed (26). However, specific compositional and structural data, necessary for the unambiguous characterization of these compounds as $(\eta-C_5H_5)_2Zr$ and $(\eta-C_5H_5)_2Hf$, were not presented.

2. Preparation of $(\eta-C_5H_5)_2Zr(2-\eta^1:1-2\eta^2-C_{10}H_7)(H)Zr(\eta-C_5H_5)_2$ (25) (4)

In an attempt to prepare a "simple" $(\eta-C_5H_5)$ zirconium metallocene, $(\eta-C_5H_5)_2ZrCl_2$ was reduced with potassium naphthalene, at $-80^\circ C$ in tetrahydrofuran, using essentially the same technique as employed for the synthesis of $\mu-(\eta^1:\eta^5-C_5H_4)(\eta-C_5H_5)_3Ti_2$ (10) (Section II,A,4). After slow warming of the reaction mixture to room temperature and suitable work-up, a dark green solid was obtained. The compound was crystallized from solutions in tetrahydrofuran, and characterized by a combination of chemical methods and single crystal X-ray crystallography as $\mu-(2-\eta^1:1-2\eta^2\text{-naphthyl})hydridobis[bis(\eta\text{-cyclopentadienyl})zirconium](Zr-Zr)$, $(\eta-C_5H_5)_2Zr(2-\eta^1:1-2\eta^2-C_{10}H_7)(H)Zr(\eta-C_5H_5)_2$ (25).



(25)

The molecule consists of a dimeric $[(\eta\text{-C}_5\text{H}_5)_2\text{Zr}]_2$ unit, with a hydrido (H) and a naphthyl (C_{10}H_7) ligand also bonded to the Zr—Zr framework [$D_{\text{Zr-Zr}} = 3.307(2)$ Å]. The unusual naphthyl ligand is bonded to both zirconium atoms. It is σ -bonded via one naphthyl ring β -carbon atom to one zirconium atom and also by an apparent η^2 -linkage via the α - and β -carbon atoms of the same naphthyl ring to the second zirconium atom. Interestingly, the η^1 :naphthyl, carbon—zirconium σ -bond is colinear with the C—H bond vector of the parent naphthalene. The hydrido ligand could not be definitively located from the crystallographic work. Its presence was demonstrated by ^1H NMR as well as by chemical reactivity studies.

In view of the expected instability of $(\eta\text{-C}_5\text{H}_5)_2\text{Zr(II)}$ systems, it is interesting that in the complex above we find “normal” bis(η -cyclopentadienyl) ligands. In the synthesis of **25**, the expected rearrangement of $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}$ intermediate species to complex cyclopentadienyl hydrides is apparently avoided by the formation of this unusual naphthyl hydride complex. However, even this complex is only of marginal stability; solutions decompose on standing at room temperature giving as yet uncharacterized blue or purple zirconium hydride complexes.

Treatment of **25** with HCl gas in tetrahydrofuran yields H_2 , $(\eta\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$, and a mixture of hydronaphthalenes ($\text{C}_{10}\text{H}_{10} > \text{C}_{10}\text{H}_{12} > \text{C}_{10}\text{H}_8$). This interesting reduction of the C_{10}H_7 moiety probably occurs via a successive protonation of the relatively electron-rich naphthyl ligand. There is a parallel with the Birch reduction of aromatics, except that in this case the reducing agent is divalent zirconium. Complex **25** reacts with hydrogen giving the polymeric $(\text{C}_5\text{H}_5)_2\text{ZrH}_2$ as the main organometallic product, and naphthalene. Solutions of **25** catalyze the hydrogenation of cyclohexene to cyclohexane. Complex **25** is much less effective as a hydrogenation catalyst for cyclohexene than $\mu\text{-(}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{)}(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**).

D. Bis(η -cyclopentadienyl)titanium(III) Aryl and Alkyl Complexes

Complexes of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti(III)R}$, where R may be an aryl, η^3 -allyl, or η^2 -cyclopentadienyl group, are known. The aryl (40) and η^3 -allyl (41) complexes are prepared by reaction of bis(η -cyclopentadienyl)titanium monochloride, or dichloride, with the appropriate Grignard reagent.



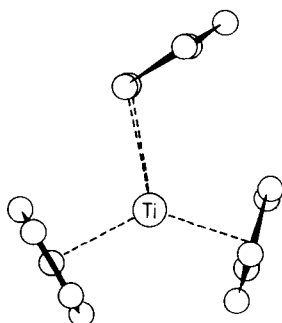
where R = C_6H_5 , *o*, *m*, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, 2,6- $(\text{CH}_3)_2\text{C}_6\text{H}_3$, 2,4,6- $(\text{CH}_3)_3\text{C}_6\text{H}_2$, C_6F_5 , $\text{CH}_2\text{C}_6\text{H}_5$



where R' = C_3H_5 , C_4H_7 , C_5H_9 .

The bis(η -cyclopentadienyl)titanium(III) aryl complexes form interesting dinitrogen derivatives (Section III,B); the 1-methyl, η -allyl complex $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^3\text{-C}_4\text{H}_7)$ is the precursor to a particularly effective homogeneous olefin hydrogenation catalyst (Section VI). Attempts to prepare bis(η -cyclopentadienyl)titanium(III) monoalkyl complexes were unsuccessful (40).

Reaction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with cyclopentadienyl sodium affords in low yield the green $(\eta^5\text{-C}_5\text{H}_5)_2(\eta^2\text{-C}_5\text{H}_5)\text{Ti(III)}$ complex (27) (42).

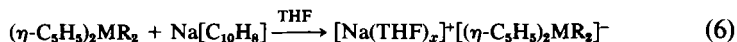


(27)¹

The molecule (27) consists of a normal, "bent" $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ moiety and an unusual η^2 -bonded, C_5H_5 ligand. The latter may be considered as a 3-electron donor ligand with the titanium adopting a 17-electron configuration (43).

¹ Reprinted with permission from Lucas *et al.* (43), *J. Chem. Soc., Chem. Commun.* p. 97 (1973). Copyright 1973 by The Chemical Society.

The anionic, dialkyltitanate, $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti(III)(R)}_2]^-$ complexes with $\text{R} = \text{CH}_3$, C_2H_5 , or C_3H_7 are formed by reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$ with excess of the alkylolithium reagent at -70°C in tetrahydrofuran (44). An apparently general procedure for preparing anionic dialkylmetallates by the sodium naphthalene (45) or potassium (46) reduction of bis(η -cyclopentadienyl)dialkyl complexes has been reported.



where $\text{M} = \text{Ti}$, Zr , or Hf and $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ or $(\text{CH}_3)_3\text{SiCH}_2$.

III

DINITROGEN FIXATION WITH LOW-VALENT TI AND Zr METALLOCENES

A. Dinitrogen Reduction Systems

The exceptional chemical inertness of dinitrogen, which is related to its high ionization potential, low electron affinity, and the abnormal strength of the $\text{N}\equiv\text{N}$ bond are well recognized. In 1964, Vol'pin and Shur (47) announced that mixtures of various transition metal compounds, e.g., CrCl_3 , MoCl_5 , TiCl_4 , and ethylmagnesium chloride in ether, react with dinitrogen to yield metal nitride species from which ammonia could be liberated by hydrolysis. It was known that dinitrogen reduces the rate of polymerization of ethylene with some Ziegler–Natta catalyst systems (e.g., TiCl_4 + diisobutylaluminum hydride) (48). It was also known that certain Ziegler–Natta catalyst mixtures, when prepared under dinitrogen, gave ammonia after hydrolysis (49). However, it was Vol'pin and Shur who, despite classical notions about the inertness of N_2 , convincingly demonstrated (using $^{15}\text{N}_2$) that dinitrogen could indeed be reduced by low-valent transition metal species formed *in situ* by reduction of metal complexes with Grignard reagents. One of the most effective reducing systems proved to be $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2 + \text{C}_2\text{H}_5\text{MgBr}$ in ether, which reacted with N_2 (150 atm), 31 h, to produce (after hydrolysis) 0.93 mol NH_3 per mole of Ti complex (50). Various combinations of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with Li, Na, K, Cs, Mg, Ce, and La likewise reduce N_2 to ammonia (51). The use of alkali metal–arene radical-anion solutions as reducing agents allows the quantitative conversion of N_2 to NH_3 even at 1 atm pressure. Thus, with the system 1:6- $(\eta\text{-C}_5\text{H}_5)_2\text{-TiCl}_2$:Li naphthalene in tetrahydrofuran, 0.96 mol NH_3 /Ti atom was obtained (after hydrolysis) after 16 h under 1 atm of N_2 (52). Titanium tetraisopropoxide and Na naphthalene mixtures are also

very effective dinitrogen reducing agents (53). The electrolytic dinitrogen reduction using low-titanium species has been demonstrated (53, 54). In these titanium-mediated N_2 -reduction systems, a maximum of 1 mol of NH_3 is obtained per Ti atom. However, various methods have been devised wherein the low-valent titanium reducing species can be partially regenerated (53) to give, in some cases, up to several hundred moles of NH_3 per mole of titanium (55). The ideal situation, wherein the titanium dinitrogen reducing agent is hydrogen gas and there is a truly catalytic hydrogenation of dinitrogen to ammonia, has never been achieved.

The various titanium mixed systems have been used not only to reduce dinitrogen to ammonia, but also to hydrazine (53) and to organonitrogen compounds. Thus, mixtures of $TiCl_4$, sodium, and naphthalene were found to give traces of naphthylamines (55). Reaction of $(\eta-C_5H_5)_2Ti(C_6H_5)_2$ with phenyllithium in the presence of N_2 gave small amounts of aniline (55). Reaction of $(\eta-C_5H_5)_2TiCl_2$ with Mg, N_2 , and diethyl ketone afforded a mixture of 3-pentylamine and di(3-pentyl)amine in 25–50% yield based on fixed N_2 (56).

Many attempts have been made to identify the low-valent dicyclopentadienyltitanium and related species responsible for the reduction of dinitrogen in these mixed systems. It was at first thought that the anionic hydride $[(\eta-C_5H_5)_2TiH_2]^-$, detected by EPR methods in the systems $(\eta-C_5H_5)_2TiCl_2/EtMgBr$; $(\eta-C_5H_5)_2TiCl_2/Li$ naphthalene, was the active N_2 -reducing species (57). However, the concentration of this hydride does not correlate with N_2 reduction (44, 52), hence it is likely that other (as yet unidentified) N_2 -reactive, low-valent titanium complexes are involved. Although several mechanisms have been proposed for dinitrogen fixation by the Vol'pin and Shur and related systems, the subject is still a matter of controversy (2, 58, 59). From conductimetric studies by Olivè and Olivè, it appears that *ionic*, low-valent titanium organometallics are involved (52). Labeling experiments have shown that at least some of the hydrogens in the ammonia formed from $N_2/(\eta-C_5H_5)_2TiCl_2/EtMgBr$ and $N_2/(\eta-C_5H_5)_2TiCl_2/Na$ naphthalene systems come from the protons of the cyclopentadienyl ligands (60). Some involvement of hydrogens of the solvent can occur but it is apparently minimal (61). Further insight on the nature of these N_2 -reducing systems has been gained by the isolation of various titanium dinitrogen complexes.

B. Aryldicyclopentadienyltitanium(III) Dinitrogen Complexes

The first transition metal dinitrogen complex, $[Ru(NH_3)_5N_2]P^+$, was prepared by Allen and Senoff in 1965 (62). By 1970, some 20 dinitrogen

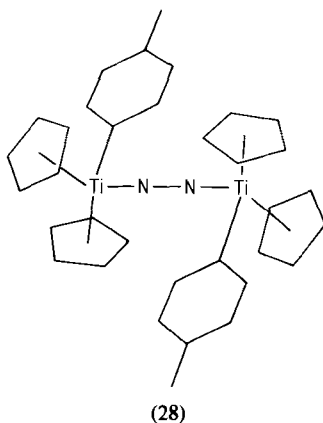
complexes were listed in a review by Chatt (63). However, none of these could be reduced to NH_3 ; the N_2 ligand in the complexes appeared to be as refractory as free N_2 gas. On the other hand, the Vol'pin and Shur and related titanium systems were known to readily reduce dinitrogen, yet (up to late 1969) no titanium dinitrogen complexes had been isolated!

1. Preparation and Structure of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiR}]_2\text{N}_2$ Complexes

Teuben and de Liefde Meijer (64) prepared the first well-characterized titanium dinitrogen complex. They found that toluene solutions of phenyl-dicyclopentadienylyltitanium(III) (26) when cooled under N_2 gave an intense blue coloration ascribed to the reversible formation of a dinitrogen adduct.



Slow cooling of solutions of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti(III)C}_6\text{H}_5$ (26) in toluene gave glittering purple crystals of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiC}_6\text{H}_5]_2\text{N}_2$. A variety of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti(III)R}$ complexes react in this manner with N_2 : for example, where R is C_6H_5 , *o*-, *m*-, *p*- $\text{CH}_3\text{C}_6\text{H}_4$, $-\text{CH}_2\text{C}_6\text{H}_5$, and $-\text{C}_6\text{F}_5$. The blue dinitrogen complexes are not formed, however, when there are steric constraints: for example, when $\text{R} = 2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3$, $2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2$, C_5H_5 (presumably 27) (65). The *para*-tolyl complex, $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(p\text{-CH}_3\text{C}_6\text{H}_4)]_2\text{N}_2$ (28), has recently been characterized by single crystal X-ray crystallography (66).

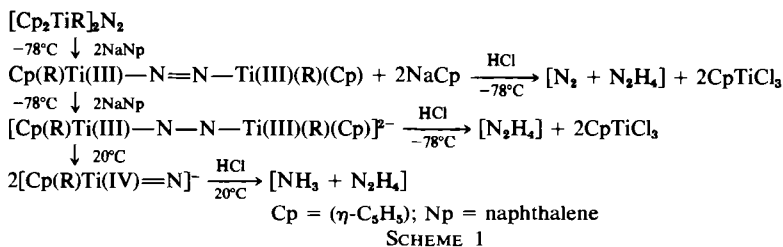


Complex 28 consists of two $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(p\text{-CH}_3\text{C}_6\text{H}_4)$ units bridged by a dinitrogen ligand, in an essentially linear $\text{Ti}-\text{N}\equiv\text{N}-\text{Ti}$ arrangement.

The N—N bond distance of 1.162(12) Å is significantly longer than that in free N₂ (1.0976 Å), although the typical N=N double bond length of 1.24 ± 1 Å is not reached. There is a somewhat distorted tetrahedral arrangement of the four ligands around titanium. A very interesting feature of the structure is the presence of a plane defined by the Ti, N, and C atoms of the *para*-tolyl group. This makes possible the delocalization of π -electrons of the N₂ ligand over the two titanium atoms and *para*-tolyl ligands.

2. Dinitrogen Reduction with $[(\eta\text{-C}_5\text{H}_5)_2\text{TiR}]_2/\text{Na-Naphthalene}$ Systems

Thermolysis of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiR}]_2\text{N}_2$ compounds results in loss of N₂; however, some nitrogen is retained in the residue and is detected as ammonia and hydrazine after hydrolysis (67). The $[(\eta\text{-C}_5\text{H}_5)_2\text{TiR}]_2\text{N}_2$ complexes liberate N₂ quantitatively with solvolysis, or treatment with H₂ (no NH₃ is produced) (64). However, reduction with excess sodium naphthalene in tetrahydrofuran yields up to 2 mol of NH₃ per mole of complex after hydrolysis. Careful studies of the reduction of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiR}]_2\text{N}_2$ with sodium naphthalene (NaNp) at -78°C indicate a very plausible scheme for the reduction of dinitrogen (68). Initial reaction leads to a loss of a cyclopentadienyl group and the formation of a diimide intermediate. The fact that one ($\eta\text{-C}_5\text{H}_5$) ligand is lost is indicated by the isolation of $(\eta\text{-C}_5\text{H}_5)\text{TiCl}_3$ from reaction of the mixture at this stage, with HCl. Further reduction gives a hydrazine precursor, as shown in Scheme 1.



Further work is needed to actually isolate and characterize some of these proposed intermediates in the reduction of dinitrogen.

3. Preparation of Related $(\eta\text{-C}_5\text{H}_5)_2\text{M(III)(alkyl)}$ ($\text{M} = \text{Ti, Zr}$) Dinitrogen Complexes

A bis(η -cyclopentadienyl)titanium(III) alkyl dinitrogen complex was prepared by reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$ with isopropylmagnesium chlo-

ride at low temperatures under N_2 . The deep blue complex decomposed at -70°C with evolution of N_2 and was thus not well-characterized (69).

Recently, the preparation of two bis(η -cyclopentadienyl)zirconium(III) dinitrogen complexes has been reported (70, 71). Reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{Cl})\text{R}$ [$\text{R} = (\text{Me}_3\text{Si})_2\text{CH}$] with sodium amalgam under N_2 gave $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{N}_2)\text{R}$ as a dark brown, paramagnetic, crystalline solid, stable under dinitrogen. There are indications that in this complex there may exist a sideways-bonded dinitrogen. In vacuum at 20°C , $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{N}_2)\text{R}$ slowly loses dinitrogen giving the purple, diamagnetic $[(\eta\text{-C}_5\text{H}_5)_2\text{ZrR}]_2\text{N}_2$. The latter complex is very likely an N_2 bridging dimer, by analogy with the blue $[(\eta\text{-C}_5\text{H}_5)_2\text{TiR}]_2\text{N}_2$ complexes, described above (e.g., compound 28). An intriguing feature of this system is the apparent specificity, associated with the $(\text{Me}_3\text{Si})_2\text{CH}$ ligand: analogous complexes, $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{III})\text{R}$, with less bulky ligands such as neopentyl or Me_3Si - do not lead to incorporation of dinitrogen. A possible reason for this may be that the bulky ligands help to maintain the cyclopentadienyl ligands of the $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}(\text{III})$ fragment intact during the reductive dehalogenation reaction with sodium amalgam.

C. Synthesis of Titanocene-Based Dinitrogen Complexes

1. Formation of Reversible "Titanocene- N_2 " Complexes

Van Tamelen and co-workers (72) were the first to report evidence for the formation of a $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ -based dinitrogen complex, prepared by exposure of solutions of "titanocene" in benzene to N_2 . An N—N vibrational stretching frequency of 1960 cm^{-1} was claimed, although it was not confirmed using $^{15}\text{N}_2$. Explicit details regarding the composition, purity, and structure of the "titanocene" used were not given. Since this "titanocene" was prepared by the method of Watt, Baye, and Drummond (16), it probably consisted mainly of the hydride complex $\mu\text{-(}\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8\text{)-}\mu(\text{H})_2\text{-(}\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$ (3) (Section II,A,1 and 2). The latter is coordinatively saturated and it seems unlikely that it should react with N_2 . Even in the light of considerable later work on $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ -based dinitrogen complexes, the composition and identity of this reversible "titanocene"- N_2 adduct in benzene with $\nu_{\text{N-N}} = 1960\text{ cm}^{-1}$ remain unclear.

Van Tamelen and co-workers (25) later reported the formation of a deep blue dinitrogen complex, $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$, prepared by reaction of their "highly unstable," "active titanocene" $[(\text{C}_5\text{H}_5)_2\text{Ti}]_{1-2}$ (8) with N_2 . Since the latter complex (8) was not adequately characterized (Section II,A,5),

the definitive composition of this dinitrogen derivative and its relationship to other blue dinitrogen complexes (i.e., **28**, **29**, and **32**) are not known at the present time.

Evidence for another dicyclopentadienyltitanium-based dinitrogen complex was obtained by Shilov and co-workers (73) in 1969. Solutions of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ and EtMgBr , when cooled to -70° to -100°C under N_2 , gave a deep blue coloration ascribed to the (reversible) formation of an N_2 complex, with a characteristic absorption at 600 nm. It appears that this complex was too unstable for proper characterization. However, hydrolysis at low temperatures gave hydrazine, and the complex was reasonably postulated as being an intermediate in the reduction of dinitrogen in the Vol'pin and Shur systems.

The dimeric, "metastable titanocene," $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$ (**7**), prepared by Brintzinger and co-workers (Section II,A,3) reacts with N_2 to give a deep blue complex claimed to have the composition $[\eta\text{-(C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ (**29**). This reactivity with dinitrogen is very striking but, unfortunately, the initial "metastable titanocene" **7** was not adequately characterized (Section II,A,3). Therefore, the stated composition of this deep blue dinitrogen derivative **29** is somewhat doubtful. Confirmatory work to characterize definitively these materials formulated as $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2$ (**7**) and $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ (**29**) is badly needed.

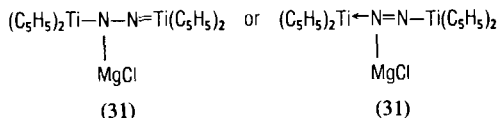
2. Complexes Containing a Highly Reduced Ligating Dinitrogen

Borod'ko and Shilov *et al.* (74–76) have reported the preparation of several paramagnetic dicyclopentadienyl dinitrogen complexes which are very interesting in that they display unusually low $\nu_{\text{N-N}}$ vibrational stretching frequencies. Reaction of $[(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$ in ether with CH_3MgI ($\text{Mg}:\text{Ti} = 2:1$) at -70°C , followed by admission of N_2 , gave a dark, nitrogen-containing precipitate which (unlike the blue complexes of references 69 and 73) was found to be stable at room temperature. Elemental analyses indicated the formula $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ (**30**) although (in the brief communication) no criteria for the purity of the composition were given (74). In a later publication (75), the complex (**30**) was said to contain some titanium hydride as an impurity. One of the authors (Shilov) now believes that the composition of this N_2 complex may not be as stated, and that, in view of the work on N_2 -reduction by $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{aryl})$ complexes (Section III,B,2), loss or exchange of a $(\eta\text{-C}_5\text{H}_5)$ ligand may have occurred during the preparation of **30** (59). We note also that this "dark precipitate" (**30**) has the same formula as the blue $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ (**29**) reported by Brintzinger *et al.* The relationship between these two dinitrogen complexes is by no means clear. The compounds are certainly different,

at least judging by their infrared spectra. They may well have far more complex structures than indicated by their given formulas, as evidenced by recent structural work on a crystalline dinitrogen derivative of μ -(η^1 : η^5 -C₅H₄)(η -C₅H₅)₃Ti₂ (**10**) (Section III,D). Obviously, much further work is needed to determine properly the composition and structure of these various "[C₅H₅)₂Ti]₂N₂" complexes.

Despite its compositional uncertainty, the "dark precipitate," [C₅H₅)₂Ti]₂N₂ (**30**), is of considerable interest since it displays an unusual ν_{N-N} infrared absorption band at 1280 cm⁻¹. The band is shifted to 1240 cm⁻¹ when ¹⁴N₂ is substituted by ¹⁵N₂. This 1280 cm⁻¹ absorption is considerably lower than the corresponding ν_{N-N} infrared absorption band of most other dinitrogen complexes and implies that in **30** there is a very significant lengthening of the N—N linkage from that in free dinitrogen (ν_{N-N} for N₂ = 2331 cm⁻¹). The ν_{N-N} = 1280 cm⁻¹ stretching frequency is intermediate between that of azobenzene [ν_{N-N} = 1441 cm⁻¹ (Raman)] (77) and hydrazine [ν_{N-N} = 1111 cm⁻¹ (Raman)] (78). The complex also shows unusual magnetic properties: the temperature dependence of the observed paramagnetism has been interpreted as arising from a partial antiferromagnetic coupling between two Ti(III) centers, possibly via a dinitrogen linkage (75). The "activation" of dinitrogen in the complex is borne out by chemical reactivity studies. Treatment of solutions of this [C₅H₅)₂Ti]₂N₂ (**30**) with HCl in diethyl ether at -60°C gives N₂, ammonia, and traces of hydrazine (74). These would be the expected products in the disproportionation of a diimine (N₂H₂) intermediate that might be formed by protonation of an "azo" dinitrogen ligand.

The preparation of another (also paramagnetic) dinitrogen complex, [C₅H₅)₂Ti]₂N₂MgCl (**31**), was subsequently reported from reaction of isopropylmagnesium chloride and (η -C₅H₅)₂TiCl₂ with N₂ in diethyl ether at -60°C (76). The complex shows an ν_{N-N} absorption at 1255 cm⁻¹ (1215 cm⁻¹ with ¹⁵N₂), which is even lower than that for [C₅H₅)₂Ti]₂N₂ (**30**). Elemental analyses and vibrational data were said to be consistent with these proposed structures:

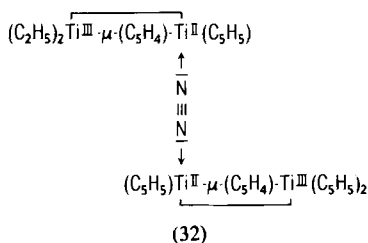


Interestingly, the complex gives mostly hydrazine upon hydrolysis (HCl in ether, -60°C). It certainly represents a very reduced state of dinitrogen. However, the actual structure of the compound may be much more

complex than the formulation above, particularly with respect to the disposition of the $(C_5H_5)_2$ rings and the possible presence of metal alkyl functions. Again, much further work is needed to characterize these very interesting "azo"-dinitrogen dicyclopentadienyltitanium-based complexes.

D. Reactivity of $\mu-(\eta^1:\eta^5-C_5H_4)(\eta-C_5H_5)_3Ti_2$ (**10**) with Dinitrogen

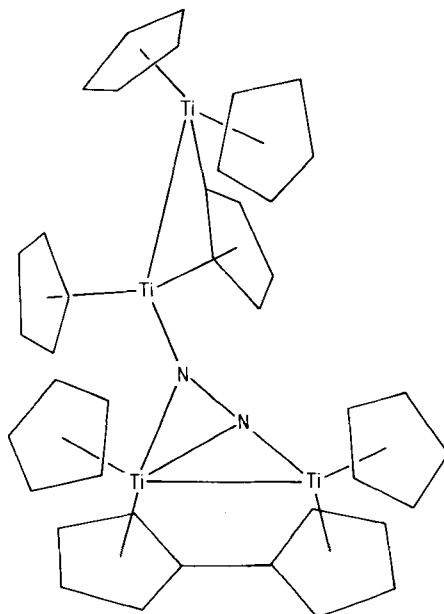
The title compound (Section II,A,4) reacts readily with dinitrogen. A number of different N_2 complexes can be obtained, depending on the reactions conditions, particularly on the type of solvent used. Solutions of **10** in relatively nonpolar solvents (e.g., benzene, toluene, hexane, diethyl ether) react reversibly with N_2 forming a deep blue complex of composition $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$ (**32**) (20). Metallocene **10** is extremely sensitive toward N_2 : saturated solutions of **10** in toluene give the blue coloration upon exposure to as little as 3 mm Hg pressure of N_2 at $-80^\circ C$! It should be noted that the $4Ti:N_2$ stoichiometry in this complex is in contrast to the $2Ti:N_2$ stoichiometry for the two other "blue" titanium dinitrogen complexes: $[(C_5H_5)_2Ti]_2N_2$ (**29**) and $[(\eta-C_5H_5)_2TiR]_2N_2$ (**28**). None of the "blue" dinitrogen complexes show a ν_{N-N} absorption in the infrared. A reasonable (probably centrosymmetric) structure for **32** may be one where N_2 binds intermolecularly between the two formally divalent titanium centers.



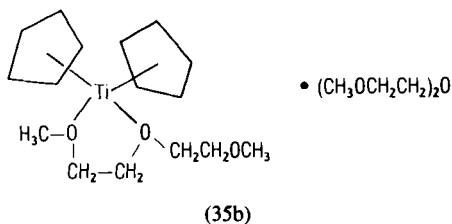
The $Ti(III)$ centers could conceivably bind the N_2 , as does the $Ti(III)$ unit in $[(\eta-C_5H_5)_2TiR]_2N_2$ (**28**). However, this is considered less likely since the blue complex does not form in tetrahydrofuran solutions. This solvent blocks the $Ti(II)$ site (as in **12**), and moreover $(\eta-C_5H_5)_2Ti(C_5H_5)$ (presumably **27**) does *not* react with dinitrogen (Section III,A,1).

In relatively polar ether solvents (glyme, tetrahydrofuran), $\mu-(\eta^1:\eta^5-C_5H_4)(\eta-C_5H_5)_3Ti_2$ (**10**) reacts under N_2 pressure to give a variety of dif-

ferent dinitrogen derivatives (79). Reaction of **10** ["crude" material—as obtained directly from the low-temperature reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$) (Section II,A,4)] with dinitrogen (10 atm) in glyme at first yields a deep blue complex (presumably **32**) and then, after further reaction (18 h, 15–20°C), a green solution and a dark precipitate are formed. The latter was shown to be a dinitrogen complex (**33**) having a characteristic $\nu_{\text{N-N}}$ absorption at 1222 cm^{-1} , which was shifted to 1182 cm^{-1} when the compound was prepared with $^{15}\text{N}_2$. The dark precipitate (**33**) dissolves in tetrahydrofuran, giving a reddish complex (**34**) with $\nu_{\text{N-N}} = 1296\text{ cm}^{-1}$ (1252 cm^{-1} with $^{15}\text{N}_2$). The latter (**34**) was also prepared directly by reaction of **10** with N_2 (10 atm) in tetrahydrofuran. A crystalline dinitrogen complex was obtained by slow diffusion of isopentane into solutions of **34** in diglyme. The crystalline complex (**35**) was thoroughly characterized by a combination of chemical methods and single crystal X-ray crystallography. It consists of two (apparently) independent molecules: (a) an N_2 complex $\mu\text{-(}\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8\text{)}(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2\text{N}_2\text{-}\mu\text{-(}\eta^1\text{:}\eta^5\text{-C}_5\text{H}_4\text{)}(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**35a**) and (b) a titanocene unit associated with two molecules of diglyme $(\eta\text{-C}_5\text{H}_5)_2\text{-Ti(C}_6\text{H}_{14}\text{O}_3\text{)}\cdot\text{C}_6\text{H}_{14}\text{O}_3$ (**35b**).



(35a)



The dinitrogen ligand in **35** is coordinated simultaneously to *three* titanium atoms. It is essentially σ -bonded to the one, formally divalent titanium atom in a molecule of $\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**) (the starting material). It is also bound, approximately in a ($\sigma + \pi$) fashion, to the two titanium atoms of a fulvalene-dicyclopentadienyl ditanium structure, $\mu-(\eta^5:\eta^5\text{-C}_{10}\text{H}_8)(\eta\text{-C}_5\text{H}_5)_2\text{Ti}_2$. The latter is essentially the structure of **3**, less the two bridging hydride atoms. This simultaneous coordination of the dinitrogen ligand to three, formally divalent titanium atoms results in a considerable chemical modification of the dinitrogen. The observed N—N bond length of 1.301(12) Å is intermediate between that of a typical N=N double bond (1.24 ± 1 Å) (80) and that of a typical N—N single bond (1.44 ± 4 Å) (80). This lengthening of the N—N linkage is also reflected in the observed $\nu_{\text{N-N}}$ frequency of 1282 cm^{-1} for the complex (1240 cm^{-1} with $^{15}\text{N}_2$).

In view of these results it now appears that the various titanium dinitrogen complexes having very low $\nu_{\text{N-N}}$ vibrational frequencies—i.e., $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2$ (**30**), $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{N}_2\text{MgCl}$ (**31**), and also complexes **33** and **34** above—may in fact have more complicated structures than previously realized. The remarkable degree of dinitrogen reduction (as implied by the low $\nu_{\text{N-N}}$ frequencies) is very likely achieved by a multiple coordination of the N_2 ligand onto three (or more) titanium atoms. The elucidation of the specific structures of these dinitrogen complexes by single crystal X-ray crystallography remains an important, challenging problem in structural and synthetic chemistry.

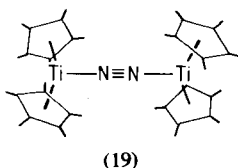
For the red crystalline dinitrogen complex **35**, the modification of the dinitrogen by coordination is seen not only in the elongated N—N bond distance but also in its chemical properties. Reaction of solutions of **35** in tetrahydrofuran with HCl gas give N_2 and small amounts of ammonia. On the other hand, hydrolysis of **35** (in tetrahydrofuran) yields mostly ($\sim 80\%$) ammonia. Some dinitrogen and traces of hydrazine are also formed. Unfortunately, treatment of **35** with hydrogen gas results in the displacement of most of the ligated dinitrogen. The use of mild reductants (for example, hydrogen-transfer catalysts) as possible H_2 -based reducing agents has yet

to be explored. The relevance of **35** to possible titanium-based catalytic dinitrogen fixation systems will be discussed in Section IV.

E. Dinitrogen Derivatives of Permethyltitanocene and Permethylzirconocene

1. Reactivity of $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Ti}$ (**16**) with Dinitrogen

The dinitrogen complex $[(\eta\text{-C}_5[\text{CH}_3]_5)_2\text{Ti}]_2\text{N}_2$ (**19**) has been prepared as blue-black needle-shaped crystals by slow diffusion of N_2 into a pentane solution of permethyltitanocene, $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Ti}$ (**16**), at 0°C (81). The complex can also be made from reaction of N_2 with pentane solutions of the partially dehydrogenated permethyltitanocene dihydride $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{TiH}_2$ (**15**); this method avoids the necessity of first isolating permethyltitanocene, $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Ti}$ (**16**). Crystalline $[(\eta\text{-C}_5[\text{CH}_3]_5)_2\text{Ti}]_2\text{N}_2$ (**19**) is moderately soluble in hydrocarbons and ether, giving dark blue solutions with characteristic absorptions in the visible at 512 and 642 nm ($\epsilon > 10^3$) (32). The structure of the complex has been elucidated by single crystal X-ray crystallography (81). The complex crystallizes as two crystallographically independent molecules of $[(\eta\text{-C}_5[\text{CH}_3]_5)_2\text{Ti}]_2\text{N}_2$ (**19**).



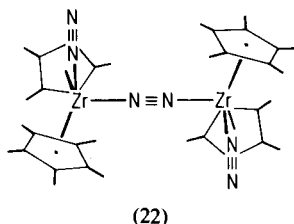
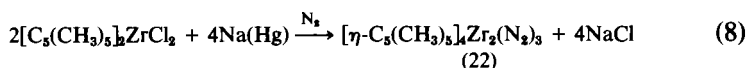
In the structure of **19**, a key feature is the apparently linear $\text{Ti}-\text{N}\equiv\text{N}-\text{Ti}$ arrangement with an average $\text{N}-\text{N}$ distance (for the two crystallographically independent molecules in the unit cell) of $1.160(7) \text{ \AA}$. This distance is very similar to the $1.162(12) \text{ \AA}$, $\text{N}-\text{N}$ bond length in the $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}](p\text{-CH}_3\text{C}_6\text{H}_4)]_2\text{N}_2$ (**28**) complex, which also displays a linear $\text{Ti}-\text{N}\equiv\text{N}-\text{Ti}$ arrangement (see Section III,B,1). For the two complexes **19** and **28**, the $\text{N}-\text{N}$ distance is significantly longer than in dinitrogen ($D_{\text{N}-\text{N}} = 1.0976 \text{ \AA}$), but it is less than the $1.24 \pm 1 \text{ \AA}$ for a typical $\text{N}=\text{N}$ double bond. Whereas $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}](p\text{-CH}_3\text{C}_6\text{H}_4)]_2\text{N}_2$ (**28**) and $[(\text{C}_5\text{H}_4)(\text{C}_5\text{H}_5)_3\text{Ti}]_2\text{N}_2$ (**32**) are reducible with sodium naphthalene to ammonia (Sections III,B and D), the bispermethyltitanocene dinitrogen complex **19** is not reducible, at least with sodium amalgam. However, proto-

nolysis of **19** with HCl gives small amounts of NH_3 (<5%) as well as H_2 and N_2 .

Upon cooling toluene solutions of $[(\eta\text{-C}_5\text{[CH}_3\text{]}_5)_2\text{Ti}]_2\text{N}_2$ (**19**) to below -10°C under N_2 , there is a color change from blue to intense purple-blue. A dark purple precipitate was obtained by cooling concentrated solutions of $[(\eta\text{-C}_5\text{[CH}_3\text{]}_5)_2\text{Ti}]_2\text{N}_2$ to -80°C , under dinitrogen. The purple precipitate obtained proved to be unstable (even as a solid) upon warming to room temperature. From measurements based upon the observed evolution of dinitrogen upon warming, this dark purple material was initially formulated as $[\text{C}_5(\text{CH}_3)_5]_2\text{TiN}_2$ (**32**). Various spectral data were cited as evidence for the presence of an equilibrium between an "end on" (i.e., η^1) and sideways-bonded (i.e., η^2) dinitrogen ligand in this complex (**82**). Also, the presence of a transient yellow-brown $[(\text{C}_5\text{[CH}_3\text{]}_5)_2\text{Ti}](\text{N}_2)_2$ complex was claimed. In subsequent work, it was shown that the composition $[\text{C}_5(\text{CH}_3)_5]_2\text{TiN}_2$, assigned the dark purple species, is incorrect. There is thus now no evidence for the earlier claim of a sideways-bonded dinitrogen in the complex. Bercaw and co-workers (**81**) now believe that this purple-blue species formed by reaction of $[(\eta\text{-C}_5\text{[CH}_3\text{]}_5)_2\text{Ti}]\text{N}_2$ with dinitrogen at low temperatures is actually $[(\eta\text{-C}_5\text{[CH}_3\text{]}_5)_2\text{Ti}]_2(\text{N}_2)_3$. The latter is considered as being analogous in composition (and presumably in structure) to the zirconium dinitrogen complex $[\eta\text{-C}_5(\text{CH}_3)_5]_4\text{Zr}_2(\text{N}_2)_3$ (**22**).

2. Preparation and Properties of $[\eta\text{-C}_5(\text{CH}_3)_5]_4\text{Zr}_2(\text{N}_2)_3$ (**22**)

Reduction of a toluene solution of bis(η -pentamethylcyclopentadienyl)zirconium dichloride with sodium amalgam under dinitrogen yields the permanganate-red colored dinitrogen complex **22** (**33**)



The structure of **22** (**83**) consists of a linear $\text{Zr}-\text{N}\equiv\text{N}-\text{Zr}$ arrangement, with $D_{\text{N-N}} = 1.182(5)$ Å. Each zirconium atom is also coordinated by an end-bound dinitrogen [$D_{\text{N-N}} = 1.116(8), 1.114(7)$ Å]. The characteristic $\nu_{\text{N-N}}$ stretching frequencies for the bridging and the two terminal dinitro-

gens are seen at 1556 cm^{-1} , 2041 cm^{-1} , and 2006 cm^{-1} , respectively. The most interesting property of the complex is the quantitative conversion of one mole of dinitrogen per mole of complex to hydrazine, upon protonolysis:



It might be expected that, in this reaction, it should be the more tightly bound bridging dinitrogen ligand that is protonated. However, labeling studies (84) have shown that approximately one-half of the N_2H_4 comes from the bridging N_2 ligand, while the remainder of the hydrazine comes from the nitrogen atoms of the terminal N_2 ligands. The authors have interpreted these results by a scheme which involves the initial protonolysis of the terminal N_2 ligands, followed by generation of a symmetric reaction intermediate, $[\text{C}_5(\text{CH}_3)_5]_2\text{Zr}(\text{N}_2\text{H})_2$, which can then be further protonated to yield hydrazine.

3. Comparison of the Chemistry of $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{M}$ versus $(\eta\text{-C}_5\text{H}_5)_2\text{M}$ ($\text{M} = \text{Ti}, \text{Zr}$) Systems

Both the permethylmetallocene and the cyclopentadienyl metallocene, low-valent titanium and zirconium systems are extremely reactive, primarily because of their electron-deficient "carbenoid" character (Section I,B). Generally speaking, there are a number of important differences vis-à-vis the chemistry of the $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{M}$ and $(\eta\text{-C}_5\text{H}_5)_2\text{M}$ ($\text{M} = \text{Ti}, \text{Zr}$) systems.

Of the divalent metallocenes, only permethyltitanocene, $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{-Ti}$ (**16**), has actually been isolated. Titanocene, $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ (**1**), is not known as a discrete species; the nearest approach to titanocene appears to be the $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{diglyme})\cdot\text{diglyme}$ unit found in the red crystalline dinitrogen complex **35** (see structure **35b**, Section III,D). Permethylzirconocene, $[\eta\text{-C}_5(\text{CH}_3)_5]_2\text{Zr}$, may exist in the solution remaining after removal of N_2 from $[(\text{C}_5[\text{CH}_3]_5)_2\text{Zr}]_2(\text{N}_2)_3$ (Section II,B,2), but this has not yet been adequately demonstrated. Zirconocene, $(\eta\text{-C}_5\text{H}_5)_2\text{Zr}$ (**2**), also has never been isolated or otherwise identified as a discrete species. In general, the permethylated complexes are more stable than the corresponding monomeric, $(\eta\text{-C}_5\text{H}_5)_2\text{M}$ species. This is because insertion of the divalent metal $[\text{Ti}(\text{II}), \text{Zr}(\text{II})]$ into the methyl C—H linkage of the $[\eta\text{-C}_5(\text{CH}_3)_5]$ ligand is expected to be more difficult than insertion into the inherently more acidic cyclopentadienyl $(\eta\text{-C}_5\text{H}_5)$ ligand, C—H linkage. Also the bulkiness of the permethylcyclopentadienyl ligands in $[\eta\text{-}$

$C_5(CH_3)_5]_2M$ systems makes it unlikely that unwanted rearrangements, giving more stabilized dimeric (e.g., bridging hydride) structures, will occur.

The chemistry of titanium and zirconium, bis(η -pentamethylcyclopentadienyl) systems is essentially that of *monomeric* $[\eta-C_5(CH_3)_5]_2M$ units. With the cyclopentadienyl systems, nearly all of the chemistry observed is that of *dimers*. Although the dimeric hydride $\mu-(\eta^5:\eta^5-C_{10}H_8)-\mu(H_2)-(\eta-C_5H_5)_2Ti_2$ (**3**) is coordinatively saturated and relatively unreactive, the partially unsaturated, dimeric metallocene $\mu-(\eta^1:\eta^5-C_5H_4)(\eta-C_5H_5)_3Ti_2$ (**10**) shows considerable chemical reactivity toward N_2 (Section III,D) as well as interesting catalytic properties (Section VI). The behavior of dimer units in the cyclopentadienyl systems is exemplified by the unusual naphthalene ring binding in the naphthyl hydride zirconocene derivative $(\eta-C_5H_5)_2Zr(\overline{C_{10}H_8})(H)Zr(\eta-C_5H_5)_2$ (see Section II,C). However, a more striking instance of the chemistry of metal-metal bonded dimeric metallocenes is shown in the structure of the red crystalline dinitrogen complex **35** (Section III,D). Here the N_2 ligand is coordinated simultaneously via three titanium atoms to two, dimeric metallocenes, resulting in a considerable chemical activation of the dinitrogen.

IV

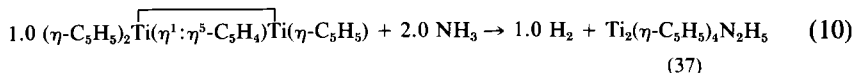
THE REACTIVITY OF LOW-VALENT TITANIUM METALLOCENES WITH NH_3 AND AMINES

A. The Homogeneous Dehydrogenation of NH_3 to Yield H_2

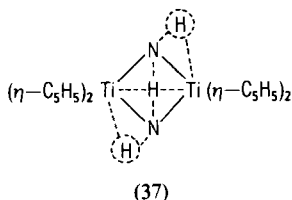
Certainly, the most striking feature of the low-valent, coordinatively unsaturated titanium and zirconium metallocenes described above is their facile reactivity with dinitrogen (Section III). This feature suggests that these metallocenes might be suitable catalysts for the reduction of N_2 by H_2 . For any catalytic cycle, the elimination of the products from the catalyst is a key factor. In the course of performing routine control experiments on the stability of **10** in the presence of NH_3 and organic amines, we were quite surprised to observe a vigorous reaction resulting in the liberation of H_2 (85–87). This section reviews our efforts to understand and use this unique, homogeneous dehydrogenation of ammonia and amines by **10** to our advantage.

1. *Preparation and Structure of an Imidohydridobis (dicyclopentadienyltitanium) Complex (37)*

Treatment of very pure **10** [crystalline **12** with the tetrahydrofuran removed (Section II,A,4)] with anhydrous NH_3 results in the vigorous, rapid elimination of hydrogen gas according to the stoichiometry (85)



The X-ray structure of **37** consists of a planar array of alternating Ti and N atoms with two $\eta^5\text{-C}_5\text{H}_5$ ligands coordinated to each Ti center. The hydrogen atoms could not be resolved in this structure, however their location is best described as shown below (37) [reprinted with permission from Armor (85), *Inorg. Chem.* **17**, 210 (1978). Copyright 1978 by the American Chemical Society].



The presence and tentative location of these hydrogen atoms was based upon the lack of a terminal $\nu_{\text{Ti-H}}$ vibration in the infrared spectrum and also on the reactivity of **37** with CH_3I or HCl . Furthermore, when **37** is treated with CO_2 , an intense $\nu_{\text{N-H}}$ vibration appears in the IR spectrum of the resulting carbamate product.

While many organometallics are well-characterized by their X-ray structure, it is often difficult to prove that a complex remains intact in solution. Compound **37** was shown to exist, in part, as a monomeric species in solution (on the basis of its apparent molecular weight in benzene, the disparity between the Vis/Near IR spectrum in the solid state versus that in solution, and the ESR spectrum in toluene) (85).

The diimide (37) reacts with CO to yield an isocyanate complex (38) (86), having a characteristic infrared absorption at 1280 cm^{-1} (88). This remarkable reaction suggests several catalytic schemes which might be useful for the synthesis of organic compounds containing the —N—C(O)— unit. This latter complex (38) could be viewed as the key intermediate in any catalytic cycle for the synthesis of isocyanates or urea from CO and NH_3 (or N_2 and H_2).² However, in our work we could not

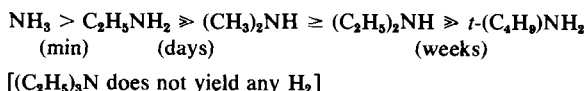
² The free energies of formation $\Delta G_{298^\circ\text{K}}^\circ$ for urea and oxamide from N_2 , CO, and H_2 are -14.2 kcal/mol and -18 kcal/mol , respectively (89, 90).

liberate a free isocyanate, nor detect any urea or oxamide on treating either amines or ammonia with CO at high pressures in the presence of **10** or **37**. Again, the bottleneck seems to be in the regeneration of the active species, which points to the strength (91) of the Ti—N bonds. Treatment of **37** with CO₂ generates another organonitrogen product, but the resulting carbamate complex cannot be recycled to regenerate an active titanium catalyst. Here, as with Bercaw's Zr/CO/H₂ systems (92), the strength of the Ti(III)–oxygen bond is the critical stumbling block in regenerating a reactive titanium complex for catalysis.

It is clear that **10** and **37** can be used to generate C—N bonds—a feature which is required for any catalytic synthesis of any organonitrogen compound; however, the resulting organonitrogen product coordinated to titanium is much too stable. It is now apparent that any attempt at a catalytic synthesis of organonitrogen compounds has to involve a metal complex which can uniquely balance all of the features outlined in Section IV,B,2.

2. Reactivity of $\mu-(\eta^1:\eta^5\text{-C}_5\text{H}_4)(\eta\text{-C}_5\text{H}_5)_3\text{Ti}_2$ (**10**) with Amines

Compound **10** in toluene also reacts with C₂H₅NH₂ to yield H₂; however, the reaction is a bit slower than that with NH₃. In fact, a variety of amines react with **10** to yield H₂ at rates which appear to be related to the size of the organic molecule (86). Relative rates of H₂ evolution are as follows:



These large differences between the rates of H₂ evolution for C₂H₅NH₂ and *t*-(C₄H₉)NH₂ suggest the importance of steric constraints associated with the approach of the amine toward the exposed metal–metal bond in **10**.

The generation of H₂ from reaction with molecules containing an N—H bond seems to be a general feature of **10**. This has also been demonstrated by the unique dehydrogenation of urea (and substituted ureas) by **10** to yield ~1 mol H₂/Ti₂ unit. The product contains a mixture of mono- and binuclear ureylene complexes, e.g., [($\eta\text{-C}_5\text{H}_5$)₂TiN(H)C(=O)N(H)Ti($\eta\text{-C}_5\text{H}_5$)₂].

The dehydrogenation of NH₃ by **10** suggests that **10** might be an active catalyst for amination reactions.³ It is remarkable that no truly effective,

³ For the reaction C₂H₄ + NH₃ → C₂H₅NH₂, $\Delta G_{298^\circ\text{K}}^\circ = -5$ kcal/mol (93). Several direct amination reactions have been observed with CO and H₂O (94), with ethylene (95), and with aromatics in very low yields (96).

catalytic route exists for the addition of NH_3 to olefins to yield primary amines (93). Yields of $\sim 70\%$ ethylamines have been reported (97) at 200°C in heptane at 860 atm of NH_3 and C_2H_4 over sodium metal. Since the diimide complex (37) can be viewed as a product of the reaction between a second molecule of NH_3 with an intermediate hydride (formed from the addition of the first molecule of NH_3 to 10), both 10 and 37 were examined as potential catalysts for the amination of olefins. Despite numerous attempts to prepare $\text{C}_2\text{H}_5\text{NH}_2$ from C_2H_4 and NH_3 at up to 136 atm and at a variety of temperatures, no catalytic synthesis of the primary amine was observed. Only traces of a mixture of primary, secondary, and tertiary amines were observed.

3. Reactivity of the Various Titanium Metallocenes with NH_3

The unique reaction of 10 with NH_3 to quantitatively produce $1.0 \text{ H}_2/\text{Ti}_2$ suggested that this reaction might be a useful probe (98) to investigate the various "titanocenes" discussed in Section II. While the fulvalene hydride (3) reacted with HCl to yield H_2 , with CH_3I to yield CH_4 , and with H_2O to yield H_2 , it reacted only slowly (over a period of days) with NH_3 to yield small amounts of H_2 . Purified preparations of 3 gave only traces of H_2 . The gray-green, polymeric hydride (6) reacted with NH_3 to yield $0.28 \text{ mol H}_2/\text{Ti}_2$. Similar reactions of the "black titanocene" (9) with NH_3 yielded only $0.15 \text{ mol H}_2/\text{Ti}_2$. This apparently incomplete elimination of H_2 from the various titanocenes reported in the early literature would tend to confirm our original suspicions that these early "titanocenes" were impure compounds and may have contained traces of 10. Again, this points to the importance of preparing crystalline materials for X-ray structural analysis in order fully to identify new complexes.

Neither the dimethyltitanocene (4) nor $(\eta\text{-C}_3\text{H}_5)_2\text{Ti}(\text{CO})_2$ (39) produced any H_2 upon treatment with NH_3 . Even the red dinitrogen complex (34) did not dehydrogenate NH_3 . This latter result is significant, because it suggests that the apparent degradative action of NH_3 upon 10 can be circumvented by preparing the dinitrogen complex. That is, one can circumvent the degradation (by NH_3) of the catalyst (10) for N_2 reduction by pressurizing the system with N_2 (98)!

B. Relevance to the Catalytic Reduction of N_2

1. Analogy of NH_3 Synthesis and Decomposition

It is interesting that compound 10, which is highly reactive toward N_2 , will also dehydrogenate ammonia. This reaction [Eq. (10)] still appears to

be unique in homogeneous systems, yet there are several heterogeneous analogies known. Elemental sodium (in the presence of iron) reacts with NH_3 giving NaNH_2 and H_2 . Atomic magnesium reacts similarly with ammonia (99). Ammonia is dissociatively chemisorbed on an iron surface yielding FeNH_2 and FeNH surface complexes and hydrogen (100). Commercial ammonia synthesis catalysts (triply promoted iron) also catalyze ammonia decomposition, into H_2 and N_2 (101). The unique capacity of **10** to dehydrogenate NH_3 may be related to its capacity to behave as a microscopic analog of a metal surface in solution. The coordinatively unsaturated titanium centers could be viewed as resembling surface metal atoms, while the $\eta^1: \eta^5\text{-C}_5\text{H}_4$ ligand in **10** would serve to poise the titanium center for reaction with incoming reagents.

2. Features of a Possible System for the Catalytic Reduction of Dinitrogen

While the mechanism for the heterogeneous synthesis of NH_3 from N_2/H_2 may not be the same as any homogeneous systems, one can try to analyze the individual steps. Certainly, these steps must involve coordination of N_2 , reduction of N_2 , and elimination of the reduced nitrogen species. With the commercial iron catalysts, the adsorption of N_2 as well as the isotopic exchange of $^{28}\text{N}_2$ with $^{30}\text{N}_2$ are affected by H_2 . Ozaki and Aika (101) have given an excellent review of heterogeneous catalysts for NH_3 synthesis. They have referred to volcano-type plots for the catalytic activity of metals for NH_3 decomposition versus the heat of formation of the highest oxide of the metal. It is clear that Fe, Ru, Os, and Mo possess features which make them effective catalysts or co-catalysts for NH_3 synthesis. We believe that it is a critical combination of the metal (1) to bind N_2 —but not too strongly, (2) to facilitate reduction by H_2 —but without displacement of N_2 , and (3) to displace the reduced nitrogen—as ammonia—with regeneration of a catalytically active form of the metal. With **10**, N_2 is coordinated, but it has not been reduced catalytically or otherwise by H_2 . The expected product of N_2 reduction, that is NH_3 , can react with the same complex (**10**) that reacts with N_2 to yield H_2 , but this complex (**37**) will not eliminate NH_3 . The latter complex (**37**), though prepared from **10** and NH_3 , will still coordinate N_2 and permit its reduction by potassium naphthalene to NH_3 (after hydrolysis). However, **37** does not catalyze the hydrogenation of this coordinated N_2 to NH_3 . Thus, there are several severe limitations to the use of titanium metallocene systems for N_2 fixation: (1) the N_2 is highly activated by coordination [as in **35a**], but yet it is still displaced by H_2 and (2) once Ti-NH_x bonds are formed (as in **37**), they cannot be broken with H_2 to yield NH_3 and regenerate an N_2 -active, low-valent titanium complex. Thus, it is likely that even if H_2 gas

could be made to reduce a titanium-based N_2 complex, the resulting $Ti-NH_x$ species might simply be too stable to result in the elimination of NH_3 and the recovery of a low-valent, N_2 -reactive titanium complex. However, systems which use two-component metal catalysts incorporating titanium might be effective.

V

π -ACCEPTOR LIGANDS COORDINATED TO TITANIUM AND ZIRCONIUM METALLOCENES

A. Carbonyl Complexes

1. Preparation and Structure of $(\eta-C_5H_5)_2M(CO)_2$ ($M = Ti, Zr, \text{ or } Hf$)

The carbonyl complexes of the group IVB metals have received a lot of attention over the last few years, because they are assumed to provide a convenient source of the carbenoid unit " $(\eta-C_5H_5)_2Ti$ " (102). Unlike most of the low-valent "titanocenes" described in Section II,A, these complexes are well-characterized, stable, and relatively easy to synthesize.

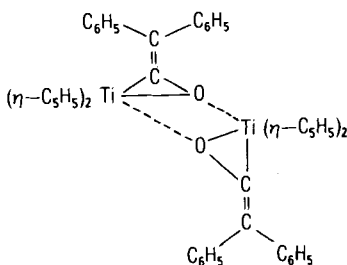
Several different procedures for the synthesis of $(\eta-C_5H_5)_2Ti(CO)_2$ (39) have been described in the literature (103, 104). This dicarbonyl complex can be easily prepared from most of the low-valent titanium metallocenes described earlier. Furthermore, 39 is quite easy to purify since it sublimates at 10^{-3} mm Hg at $80^\circ C$ to yield deep maroon crystals. Recently, Floriani (105) described a method which is applicable to the preparation of both $(\eta-C_5H_5)_2Ti(CO)_2$ as well as $(\eta-C_5H_5)_2Zr(CO)_2$ via the carbonylation of the corresponding $[(\eta-C_5H_5)_2M(BH_4)_2]$ compounds. Rausch *et al.* have published the X-ray structure of $(\eta-C_5H_5)_2Ti(CO)_2$ (106) and $(\eta-C_5H_5)_2Hf(CO)_2$ (107) as well as some information on thermal and light-induced reactions of $(\eta-C_5H_5)_2Hf(CO)_2$. The structure of 39 consists of a distorted tetrahedral array of the $\eta^5-C_5H_5$ and CO ligands around the Ti center. Unlike the Ti analog where the cyclopentadienyl ligands are eclipsed, the analogous Hf complex contains staggered cyclopentadienyl rings.

2. Reactions of $(\eta-C_5H_5)_2Ti(CO)_2$ (39)

Floriani *et al.* have studied a large number of reactions of $(\eta-C_5H_5)_2Ti(CO)_2$ (39) under the assumption that once the CO ligands are

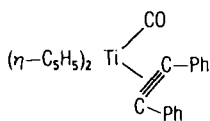
eliminated, the complex is a convenient source of “ $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$.” The dicarbonyl complex (**39**) is quite reactive with a variety of molecules such as diphenylacetylene (*108*, *108a*), diphenyl ketene (*109*, *110*), acyl halides (*102*), $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$, 9,10-phenanthraquinone (*102*), azobenzene (*111*), nitric oxide (*112*), TCNE (*113*), alkyl halides (*114*), 2,2'-bipyridine (*115*), and a variety of other compounds (2). A few illustrative examples of some of the rather remarkable products are cited below.

Diphenyl ketene reacts with **39** to yield what has been described as a “metal-anchored olefin complex” (**40**) (*109*). The latter contains a diphenyl ketene ligand which is $\eta^2\text{-C,O}$ (a metallocyclopropene) -bonded to the $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ unit. Upon treatment of **40** with protic acids, carbon mon-

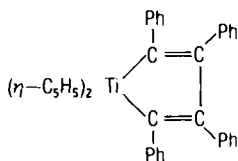


(40)

oxide, diphenylmethane, and tetraphenylethane are obtained (*110*). Diphenylacetylene reacts with the dicarbonyl (**39**) to yield an η -acetylene complex (**41**). The latter decomposes on heating (*108a*) to yield the parent dicarbonyl (**39**) and **42**.

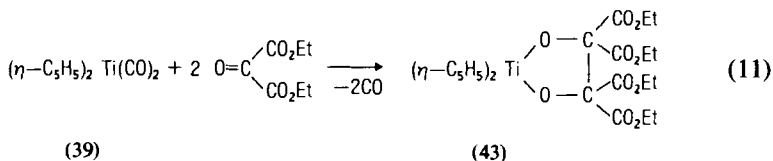


(41)

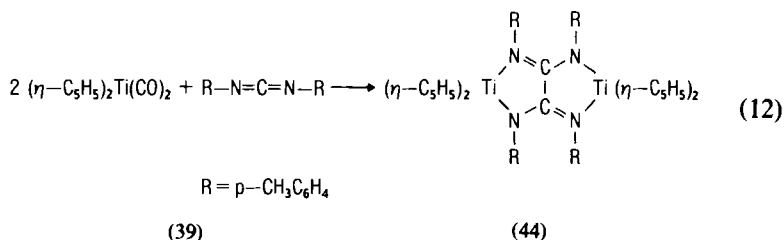


(42)

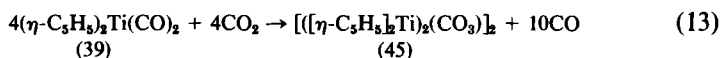
Dicarbonyl **39** is quite effective in promoting the reductive coupling of carbonyl or imino functional groups. Addition of diethyl ketomalonate to solutions of **39** yields **43** (*116*).



In a similar manner *N,N'*-di-*p*-tolylcarbodiimide reacts with **39** to yield a dimer (**44**) containing an *N,N',N'',N'''*-tetra-*p*-tolylloxalylamide derivative (116).



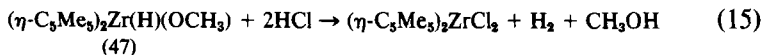
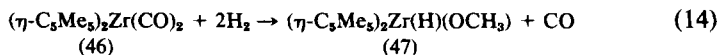
With CO₂, the titanium center of the dicarbonyl complex promotes the disproportionation of CO₂ giving CO and a tetranuclear carbonato complex of titanium(III) (117).



In complex **45** the CO₃²⁻ ligand bridges three (η-C₅H₅)₂Ti units. By way of contrast, (η-C₅H₅)₂Zr(CO)₂ reacts with CO₂ to yield a cyclic trimer [(η-C₅H₅)₂ZrO]₃. This trimer contains a six-member, nearly planar ring containing three, alternating Zr—O units (117).

3. Stoichiometric Reduction of CO by H₂ to Methanol

Bercaw and co-workers (118) have pursued some elegant syntheses and reactions of permethylated zirconocenes. They have observed the reduction of CO by H₂ to methanol when (η-C₅Me₅)₂Zr(CO)₂ (**46**) is treated with H₂.



The zirconium product, (η-C₅Me₅)₂ZrCl₂, cannot be recycled with H₂ and CO catalytically to produce **46**. Herein lies the difficulty in the use of low-valent zirconium complexes as potential catalysts for CO reactions. The affinity of Zr for oxygen donors is so great that extreme measures are required to liberate the products, resulting in the destruction of the active form of zirconium. Just as the strength of the Ti—N bonds seems to limit the catalytic incorporation of the activated dinitrogen into organic molecules (Section IV,B), so does the strength of the Zr(IV)—O bond limit the

catalytic application of Zr(II) and Zr(III) complexes where oxygen-containing donors are present. However, as Bercaw has pointed out (118), these zirconium complexes do serve as models which allow researchers to probe the mechanisms of CO/H₂ chemistry.

4. Reactivity of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ (39) with Nitrogen Oxides

It is quite remarkable that with all the effort on dinitrogen fixation with the titanium metallocene systems very little is known about the reactions of these complexes with the oxides of nitrogen. Salzmann (119) reported the formation of a polymeric complex $[(\eta\text{-C}_5\text{H}_5)_2\text{TiNO}]_x$ from the reaction of 3 and NO in toluene solutions. Later, Bottomley and Brintzinger reported that $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ (39) reacts with NO to yield $[(\eta\text{-C}_5\text{H}_5)_2\text{TiO}]_x$ as well as an apparent isocyanate complex (112). With an excess of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ to nitric oxide, CO, CO₂, N₂, and a Ti-isocyanate species were observed. With N₂O, $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ yields N₂, CO, and various Ti-oxo species. In contrast to our studies with 37 and CO, $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ and NH₃ did not generate an isocyanate species.

B. 2,2'-Bipyridyl (bipy) and Related N-Heterocyclic Complexes

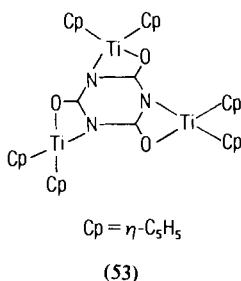
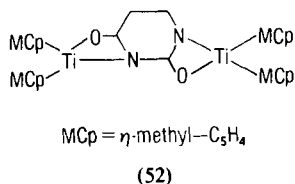
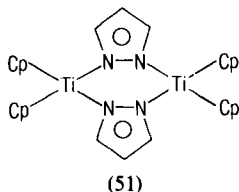
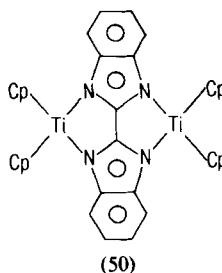
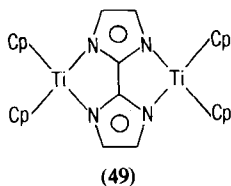
1. Preparation and Properties of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{bipy})$ (48)

The bipyridyl complex has been prepared by two different methods. When $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ is reduced with Li₂dipy, the blue-black $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{bipy})$ (48) is produced (120). Alternatively, 48 has been prepared by reaction of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ with 2,2'-bipyridine (115).

Like $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$, the analogous 2,2'-bipyridyl complex of $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ is relatively stable. However, the 2,2'-bipyridyl(bipy) complex (48) appears to have a different electronic structure (121). Unlike the dicarbonyl complex (39) which is diamagnetic, the bipy complex is weakly paramagnetic displaying an EPR signal at room temperature. One can alternatively view $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{bipy})$ (48) as containing a Ti(II) center complexed to a neutral molecule of bipy, as a Ti(III) center bound to a bipyridyl radical-anion, or as a titanium(IV) species bound to a bipyridyl dianion. Stucky *et al.* (121) have concluded that the magnetic susceptibility measurements coupled with the EPR spectra of 48 are characteristic of a d¹, Ti(III) complex which is monomeric both in solution and in the solid state.

2. Uracil and Imidazole Complexes

Fieselmann, Hendrickson, and Stucky (122–124) have prepared several Ti(III) metallocenes containing a variety of nitrogen heterocyclics. Starting with bis(cyclopentadienyl)titanium monochloride (or the analogous methylcyclopentadienyl complex), a suitable reductant, and the free ligand they were able to synthesize $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2(\text{BiIm})$ (**49**), $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{BiBzIm}$ (**50**), $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{pz})]_2$ (**51**), cyanuratotris[bis(η^5 -cyclopentadienyl)titanium(III)] (**52**), and uracilatobis[bis(η -methylcyclopentadienyl)titanium(III)] (**53**) where Pz^- = anion of pyrazole, BiIm^{2-} = dianion of 2,2'-biimidazole, and BiBzIm^{2-} = dianion of 2,2'-bibenzimidazole.



For the μ -pyrazole complex (**51**), X-ray structural analysis indicates that the pyrazole ligand is present in a 1,2- η^2 configuration (123). The four ni-

trogen atoms of the pyrazolide groups and the two Ti centers link to adopt a chairlike configuration in this six-membered heterocyclic dimer.

These complexes display some very interesting structural and magnetic properties (122–125). For the pyrazolate complex (**51**), the magnetic susceptibility measurements indicated the absence of any antiferromagnetic exchange between the Ti(III) centers. On the other hand, compounds **49** and **50**, where the metals are even further apart than in **51**, do exhibit antiferromagnetic exchange (124). While these antiferromagnetic interactions are considerably weaker than those observed for the corresponding halide-bridged compounds, this work certainly demonstrates that extended organic bridges can facilitate the antiferromagnetic interaction between two Ti(III) centers. The difference in the magnetic properties of **51** versus **49** and **50** can be attributed to the fact that, in the pyrazolate-bridged complex (**51**), the Ti(III) ions are not in the same plane formed by the two pyrazolate anions (121).

VI

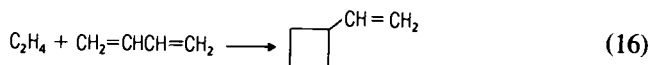
REACTIONS OF OLEFINS AND ACETYLENES CATALYZED BY LOW-VALENT Ti AND Zr METALLOCENES

A. The Isomerization of Olefins

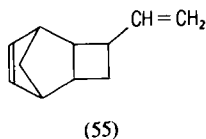
The $(C_5H_5)_3(C_5H_4)Ti_2$ complex (**10**) is an effective catalyst for the isomerization of double bonds in olefins (20). Compound **10** catalyzes the isomerization of cycloocta-1,5-diene to cycloocta-1,3-diene. The hydrogenated form of the 1-methyl- η -allyldicyclopentadienyltitanium (**54**) complex (126) also catalyzes this latter isomerization. In addition, compound **10** rapidly isomerizes terminal olefins such as 1-heptene to the more thermodynamically stable internal olefins [a mixture of *trans*- (95%) and *cis*-2-heptenes]. Also, a 0.006 *M* solution of compound **10** isomerizes 1-hexene to a mixture of ~52% *trans*- and ~4% *cis*-2-hexene, but no *trans*-3-hexene is detected (20). The effectiveness of **10** as a catalyst for isomerization of olefins can probably be attributed to a π -allyl metal intermediate whereby the isomerization occurs via a 1,3-hydrogen shift (127). Although an active catalyst for olefin hydrogenation, $[(\eta-C_5H_5)_2TiNH_2]H$ (**37**) does not promote the isomerization of 1-heptene (86). Furthermore, the tetrahydrofuran adduct of **10** (that is **12**) does not catalyze the isomerization of 1-heptene unless the solution is first heated to ~100°C (20).

B. Dimerization of Olefins

Tetrabenzyltitanium or two-component titanium catalysts of the Ziegler type have been observed to catalyze the cyclodimerization of ethylene and 1,3-butadiene to vinylcyclobutane [Eq. (16)] (128). While propylene

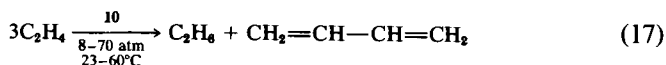


did not co-dimerize with 1,3-butadiene, strained olefins such as norbornadiene were found to co-dimerize with 1,3-butadiene to yield **55**.



Most of the titanium metallocenes described above by Cannell (128) formally start out as Ti(IV); however, he points out that the production of vinylcyclobutane is a general property of reduced organotitanium complexes having open coordination sites. In all probability, the catalysis is effected by low-valent titanium metallocenes which are produced during the reaction.

Mixtures of $\text{Al}(\text{C}_2\text{H}_5)_3$ and $\text{Ti}(\text{O}-i\text{C}_3\text{H}_7)_4$ will dimerize ethylene to 1-butene but they do not catalyze the isomerization of the 1-butene produced (129). Under the right set of conditions, only small amounts of polyethylene are produced with this latter mixture. On the other hand, solutions of compound **10** or **3** have been found to catalytically convert ethylene to ethane and butadiene (130).

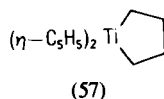


It is believed that this unique reaction is facilitated by the presence of the highly exposed and coordinatively unsaturated metal-metal bond in **10**. The activity of the fulvalene hydride (**3**) as a catalyst for this reaction is also consistent with the belief that two, adjacent titanium centers are required. The IR spectrum of **3** after the reaction with ethylene shows no Ti-H stretching vibration suggesting that a titanium-olefin derivative (rather than the hydride) is the actual catalyst.

Treating **10** with lithium powder generates a new hydride, $\text{Li}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_5\text{H}_5)\text{TiH}$ (**56**). This latter compound is ineffective for Eq. (17), but it does catalyze the dimerization of C_2H_4 to yield mainly 1-butene (131).

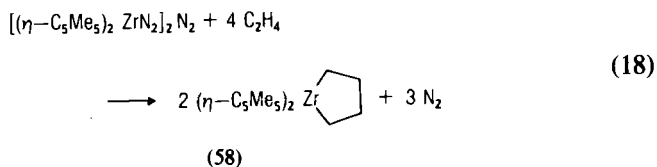
C. Formation of Metallocycles

McDermott and Whitesides (132) have reported that 1,4-dilithiobutane in ether at -78°C reacts with $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ to yield a reactive organotitanium complex stable below -30°C . They formulated the product as a metallocycle.

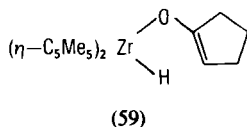


Treatment of compound **57** with CO at -50°C and warming to room temperature generated cyclopentanone (133). Reaction of the "metastable titanocene"-related compounds **6** and **29** with ethylene and subsequent treatment with CO also gave cyclopentanone, thus suggesting the possible formation of a titanium metallocycle from a $(\text{C}_5\text{H}_5)_2\text{Ti}$ fragment and ethylene. However, reaction of complex **10** with C_2H_4 and then CO did not yield cyclopentanone (134). This discrepancy probably can be attributed to the sources of "titanocene," and it should be re-emphasized that the term "titanocene" has been loosely used in the literature to represent any number of low-valent titanium metallocenes often generated from reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ (Section II,A,5).

Recently, Bercaw and co-workers (118) reported the following reaction with the permethylated zirconium complex.



Furthermore, compound **58** reacts with CO at 25°C to yield **59**.



When treated with HCl, **59** yields cyclopentanone and $(\eta\text{-C}_5\text{H}_5)_2\text{ZrCl}_2$.

Schwartz and co-workers (135) have studied a variety of zirconium(III) and zirconium(IV) metallocenes as reagents for functionalizing olefins. Recently, Gell and Schwartz (136) have described the synthesis of a di(cy-

clopentadienyl)zirconium(II)bis(phosphine) complex (**60**). This latter complex reacts with hex-3-yne or octa-1,7-diene to yield zirconium metallocycles. Complex **60** has been suggested to be "an efficient source of monomeric zirconocene" (C_5H_5)₂Zr (*136*).

D. Polymerization of Acetylene

It has been reported that a "titanocene complex" prepared by reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$ with sodium amalgam catalyzes the polymerization of acetylene (*137*). Compound **10** [directly as prepared from the low-temperature reduction of $(\eta\text{-C}_5\text{H}_5)_2\text{TiCl}_2$] is an excellent catalyst for the polymerization of acetylene (*138*). Hexane solutions of **10** when exposed to 1 atm of C_2H_2 yield a deep red, solvent-swollen polymer (*138*). This mass of product was vacuum dried to yield a metallic gray, bulk polymer. When the reaction was carried out at -80°C , a *cis*-rich polymer was obtained. However, at room temperature, a polymer having a mixture of both the *cis* and *trans* structures was isolated. Addition of I_2 to the solvent-swollen polymer in hexane (*138*) enables one to prepare a highly conducting iodine derivative of polyacetylene (*139*). Doping the *cis*-polyacetylene with $\text{FSO}_2\text{OOSO}_2\text{F}$ in SO_2F_2 solutions at low temperature generates a polymer with even greater metallic electrical conductivities ($800\ \Omega^{-1}\text{ cm}^{-1}$) (*140*). Thus, the use of **10** as a catalyst for these reactions represents a convenient method for obtaining highly crystalline (*141*) polyacetylene polymers.

E. Catalytic Hydrogenation of Olefins

Table I summarizes the application of various low-valent titanium metallocenes as catalysts for olefin hydrogenation. Compounds **10** and **37** are very effective hydrogenation catalysts for C_2H_4 and cyclohexene. Since different researchers have used widely varying conditions, we can only estimate that the polystyrene-supported " $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}$ " (*142*) is comparable in activity to compounds **10** and **37**. When one recalls that **37** was prepared by a formal oxidation of the Ti centers in **10**, it is remarkable that **37** is as good a catalyst as **10**. Solutions prepared by reaction of 1-methyl- η -allylbis(cyclopentadienyl)titanium (**54**) with H_2 do appear to be more active hydrogenation (*126*) catalysts than **10** and **37**. The dicarbonyl complex, $(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ (**39**), has been shown to be a catalyst for the hydrogenation of acetylene at ~ 50 atm of H_2 (*143*). It does not catalyze the hydrogenation of simple olefins. However, Floriani and Fachinetti discovered that if

TABLE I
RATES OF OLEFIN HYDROGENATION BY VARIOUS TITANIUM METALLOCENES*

Catalyst	$10^3[\text{Catalyst}]$ (M)	T (°C)	Substrate	[Olefin] (M)	$P_0(\text{H}_2)$ (torr)	$10^4 k$ (sec ⁻¹)	Initial rate (cm ³ of H ₂ min ⁻¹ mEq ⁻¹ of Ti)	$t_{1/2}$ (min)	Product
(C ₅ H ₅) ₃ (C ₅ H ₄)Ti ₂ ^a	8.51	20.8	Cyclohexene	9.87	550	3.81	34.2	30.3	Cyclohexane
	2.71	20.4			810	4.39	134.0	26.3	
	1.15	20.6			770	1.05	51.8	110.0	
(C ₅ H ₅) ₃ (C ₅ H ₄)Ti ₂ ^b	2.68	21.4			775	2.04	73.5	56.6	
(C ₅ H ₅) ₃ (C ₅ H ₄)Ti ₂ ^a	2.94	20.1	Cyclohexene in tetrahydrofuran	5.62	670	0.487		237.0	
Polymer-attached “(C ₅ H ₅) ₂ Ti” (I42)		R.T. ^c	Cyclohexene in cyclohexane	1.16	(760) ^d		88.7		
(C ₅ H ₅) ₂ Ti C ₄ H ₄ (CH ₃) + H ₂ (I26)	8.6	R.T. ^c	Cyclohexene in cyclohexane	1.76	(760) ^d			6.0	
(C ₅ H ₅) ₃ (C ₅ H ₄)Ti ₂ ^b	9.52	23.5	Cycloocta-1,5- diene	8.15	700	6.75		17.1	Cyclooctane
(C ₅ H ₅) ₂ (C ₁₀ H ₈)Ti ₂ H ₂ (III) ^e	24.6	25.0	Cyclohexa-1,4- diene	10.57	800	0.082		1410	Cyclohexane
	11.2	22.0	Cycloocta-1,5- diene	8.15	781	0.067		1729	Cyclooctane
[(C ₅ H ₅) ₂ TiNH] ₂ H	5.5	20.0	Cyclohexene	9.87	700	2.8 ^f		41	Cyclohexane
Ph ₃ C ₂ (CO)Ti(η-C ₅ H ₅) ₂	7.8	R.T.	Cyclohexene	0.37	(760) ^d	~12 ^g		10	Cyclohexane

^a Prepared from crystalline (C₅H₅)₃(C₅H₄)Ti₂(C₄H₈O)·(C₄H₈O) (3).

^b Product of (C₅H₅)₂TiCl₂ + 2KC₁₀H₈ reaction (3).

^c At room temperature. Exact temperature not specified.

^d Assumed to be 760 torr.

^e Prepared from (C₅H₅)₃(C₅H₄)Ti₂; see Ref. 20.

^f With (C₅H₅)₃(C₅H₄)Ti₂ under these conditions, the specific second-order rate was 0.044 M⁻¹ sec⁻¹ vs. 0.051 M⁻¹ sec⁻¹ for 37.

^g Extrapolated from data (I44) indicating 90% conversion in 14 h.

* Adapted with permission from Pez and Kwan (20), *J. Am. Chem. Soc.* **98**, 8079 (1976). Copyright 1976 by the American Chemical Society.

$(\eta\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CO})_2$ was first treated with diphenylacetylene, the product, $(\text{Ph}_2\text{C}_2)(\text{CO})\text{Ti}(\eta\text{-C}_5\text{H}_5)_2$ (**41**), is a very effective hydrogenation catalyst for acetylene as well as for olefins (*144*). It is in fact even a better olefin hydrogenation catalyst than compounds **10** and **37** (see Table I). The effectiveness of **41** and **37** for the hydrogenation of cyclohexene suggests that the low-valent, coordinatively unsaturated feature of $(\text{C}_5\text{H}_5)_3(\text{C}_5\text{H}_4)\text{Ti}_2$ (**10**) does not necessarily present an advantage in olefin hydrogenation catalysis.

Brubaker and co-workers have prepared polymer-attached $(\text{C}_5\text{H}_5)_2\text{TiCl}_2$. When reduced with butyllithium in hexane, the supported titanium complex was ~ 70 times more reactive with respect to the catalytic hydrogenation of cyclohexene as compared with the reduced, nonattached titanocene dichloride (*142*). Later, Grubbs, Law, Cukier, and Brubaker established that the rates of hydrogenation per gram of polymer-attached titanocene complex reached a maximum at a value consistent with the isolation at low loadings of the titanium complex (*145*). Attempts to use this supported titanocene for the stoichiometric reduction of N_2 to NH_3 failed. This is consistent with the fact that activation of N_2 by low-valent titanium metallocenes generally requires at least two adjacent titanium centers (Section III,D,3). While Brubaker, Grubbs, and co-workers presented convincing evidence for the importance of mononuclear complexes for olefin hydrogenation in their systems, this does not suggest that binuclear complexes are inactive. This latter feature is certainly not the case for **10** (established to be dimeric in solution), which is an active hydrogenation catalyst (*20*).

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Photochemistry of Organopolysilanes

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I

INTRODUCTION

A fascinating area of organosilicon chemistry in the past decade has been the formation and reactions of reactive silicon intermediates, such as divalent silicon species (1-5) and silicon-carbon double-bonded intermediates (6-8). Until recently most of these intermediates had been produced mainly by thermolysis of appropriate silane precursors or by reduction of silicon halides with the alkali metal. In 1964 Gilman, Atwell, and Schwebke reported that permethylated polysilanes exhibit characteristic absorptions in the ultraviolet region (9). Since this initial report, the electronic spectra of many types of organopolysilanes have been measured by several research groups (10-13). In spite of these findings, no interest was shown in the photolysis of these catenated silicon compounds until 1969 when we initiated a series of studies on the photolysis of organopolysilanes (14). Recently, however, considerable attention has been focused on

the photochemistry of these compounds, and a large number of reactive silicon intermediates have been produced photochemically (8).

The purpose of this review is to summarize the recent results, obtained mainly in our laboratory, on photochemical generation and reactions of the silylenes and silicon-carbon double-bonded intermediates.

II

PHOTOLYSIS OF ORGANOPOLYSILANES

Photochemical behavior of monosilanes has been investigated by mercury-sensitized photolysis (15-19), flash photolysis (20, 21), vacuum ultraviolet photolysis (22-27), and matrix photolysis (28-30). The first examples of the photolysis of permethylated polysilanes were published in 1970 (14). All of the cyclic and acyclic permethylpolysilanes with the exception of hexamethyldisilane readily undergo photolysis on irradiation with ultraviolet light to give shorter chain compounds with the concurrent generation of the divalent silicon intermediate, dimethylsilylene (8).

A. Cyclic Permethylpolysilanes

Photolysis of dodecamethylcyclohexasilane in cyclohexane upon irradiation with a low-pressure mercury lamp bearing a Vycor filter (Fig. 1) for 20-40 h affords two of the lower homologs, decamethylcyclopentasilane and octamethylcyclotetrasilane, with concurrent extrusion of dimethylsilylene (31). The relative rate of the photolysis is strongly dependent on the initial concentration of $(\text{Me}_2\text{Si})_6$; and the relative yields of the products also depend upon the duration of reaction, as shown in Table I. At a high concentration, the major product after 20 h irradiation is decamethylcyclopentasilane, but a relatively large amount of the starting cyclohexasilane remains unchanged. At a low concentration, the starting cyclohexasilane is converted completely to two of the lower homologs, and a small amount of the open-chain product, 1,4-dihydrooctamethyltetrasilane, is also formed. However, the hexamethylcyclotrisilane expected from ring contraction of the cyclotetrasilane is never observed in this photolysis. Prolonged irradiation of the dilute solution leads to an increased yield of the cyclotetrasilane, but the amount of the open-chain product also increases (Scheme 1). The formation of $\text{H}(\text{Me}_2\text{Si})_4\text{H}$ in significant amounts on prolonged irradiation suggests that the cyclotetrasilane undergoes homolytic scission of the silicon-silicon bond to give a diradical

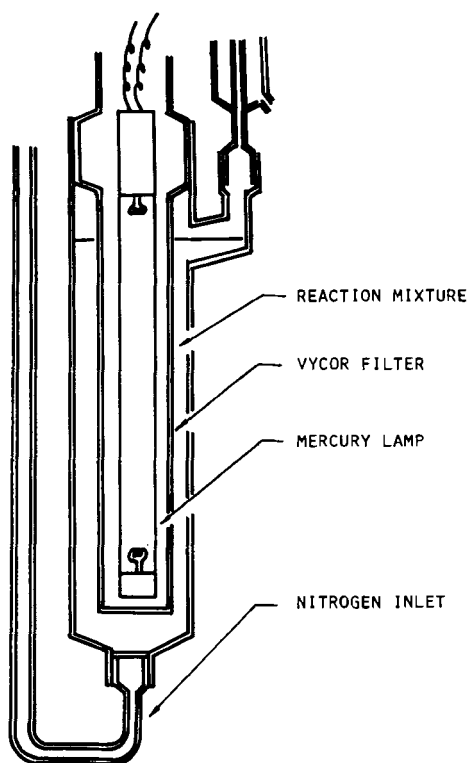
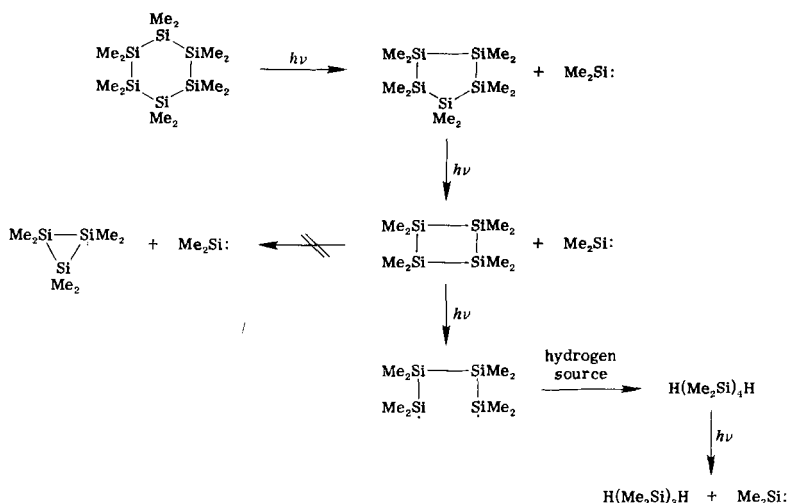


FIG. 1. Reaction vessel with a low-pressure mercury lamp.

TABLE I
PHOTOLYSIS OF DODECAMETHYLCYCLOHEXASILANE IN CYCLOHEXANE (200 ml)

(Me ₂ Si) ₆ (g)	Time (h)	Yield of volatile products (%)				Residue (g)
		H(Me ₂ Si) ₄ H	(Me ₂ Si) ₄	(Me ₂ Si) ₅	(Me ₂ Si) ₆	
8	20		3	55	40	3.0 ^a
6	20		11	67	19	2.3 ^a
4	20	Trace	12	68	17	1.7 ^a
2	20	5	17	70		1.1 ^b
2 ^c	40	14	20	52		1.0 ^b

^a Solid.^b Liquid.^c H(Me₂Si)₃H was also obtained in 3% yield.



SCHEME 1

which then abstracts hydrogen atoms from the solvent. 1,4-Dihydrooctamethyltetrasilane undergoes further photolysis with loss of dimethylsilylene to give 1,3-dihydrohexamethyltrisilane which is stable under the conditions used.

The silylene species generated during photolysis are thought to polymerize in the absence of a trapping agent. The polymeric substances thus obtained react with bromine very violently, suggesting the presence of silicon-silicon bonds. The IR spectrum of the polymeric substances shows a weak absorption at 2090 cm^{-1} due to the Si-H stretching vibration.

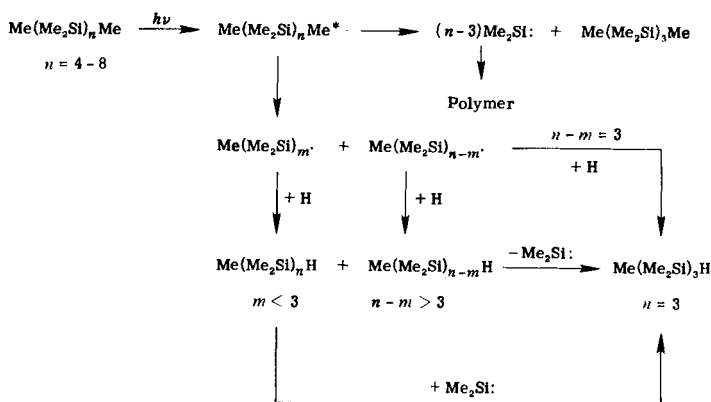
B. Linear and Branched Permethylpolysilanes

Linear permethylpolysilanes $\text{Me}(\text{Me}_2\text{Si})_n\text{Me}$ with $n = 4-8$ also undergo photolysis when their cyclohexane solutions are irradiated with a low-pressure mercury lamp (32, 33). Octamethyltrisilane is always produced as the major volatile product, in addition to 1-hydroheptamethyltrisilane and polymeric substances arising from polymerization of dimethylsilylene. Octamethyltrisilane ($\lambda_{\text{max}} 215.0\text{ nm}$) is photochemically rather stable under the conditions used, but prolonged irradiation of its dilute cyclohexane solution causes skeletal contraction, giving hexamethyldisilane with extrusion of dimethylsilylene.

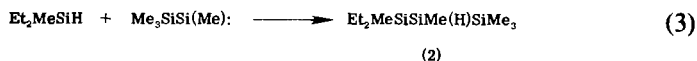
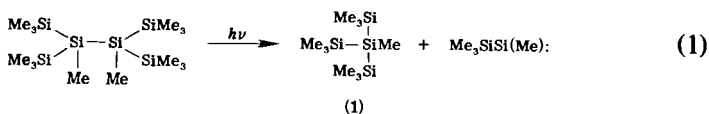
The contraction of the silicon-silicon chain of a higher polysilane molecule to give the trisilane can be explained as a result of extrusion of di-

methylsilylene. However, the formation of 1-hydropermethylopolysilanes with skeletal chain shorter than that of the starting polysilane must be ascribed to homolytic scission of the silicon-silicon bond producing silyl radicals, which immediately abstract hydrogen from solvent or other available sources. If the number of silicon atoms in the 1-hydropermethylopolysilanes thus formed is larger than three, they undergo further photolysis with the concurrent generation of dimethylsilylene. On the other hand, the hydrosilanes containing fewer than three silicon atoms react, if no trapping agent is present in the system, with dimethylsilylene to give 1-hydroheptamethyltrisilane. The photochemical pathways leading to the observed compounds may be represented by Scheme 2.

The photolysis of branched permethylopolysilanes is of considerable interest because a novel silylene intermediate, trimethylsilylmethylsilylene, is produced (34). Thus, irradiation of $[\text{Me}(\text{Me}_3\text{Si})_2\text{Si}]_2$ in the presence of diethylmethylsilane in cyclohexane affords tris(trimethylsilyl)methylsilane (**1**) and 1,1-diethyl-1,2,3,3,3-pentamethyltrisilane (**2**). Similar photolysis of **1** in the presence of diethylmethylsilane produces hexamethyldisilane and the silylene insertion product **2** in high yield.

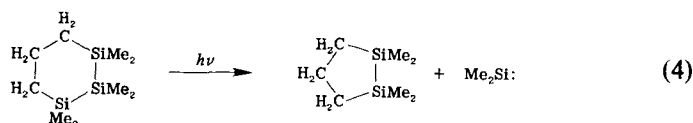


SCHEME 2

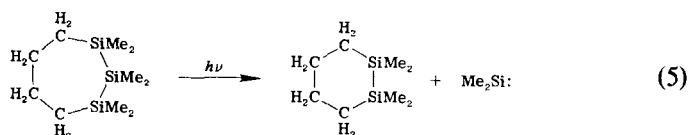


C. Polysilacycloalkanes

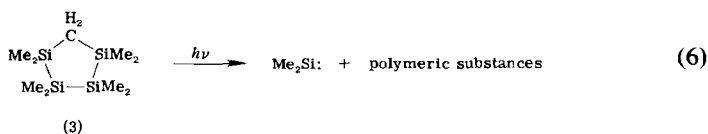
Polysilacycloalkanes with more than three silicon atoms linked together exhibit absorptions in the ultraviolet region (35, 36) and undergo photolysis to give silylene species as expected (37). Photochemical behavior of the polysilacycloalkanes depends highly on the number of a carbon atom in the polysilacycloalkane ring. Irradiation of 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclohexane in cyclohexane with a low-pressure mercury lamp affords 1,1,2,2-tetramethyl-1,2-disilacyclopentane in a high yield with loss of dimethylsilylene. Similar irradiation of 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacycloheptane gives silylene species, along with 1,1,2,2-tetramethyl-



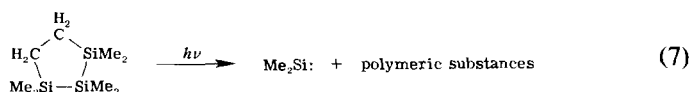
1,2-disilacyclohexane which is photochemically stable (37, 38). Photolysis



of 1,1,2,2,3,3,4,4-octamethyl-1,2,3,4-tetrasilacyclopentane (3) also produces dimethylsilylene; however, no trace of the four-membered ring compound that one would expect can be detected. Thus, irradiation of 3

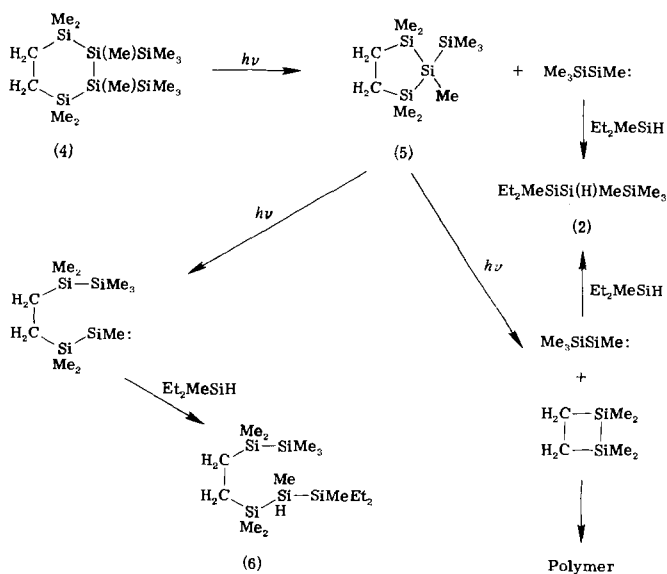


in the presence of a large excess of diethylmethylsilane gives only the silylene insertion product as a volatile substance. The photochemical behavior of 1,1,2,2,3,3-hexamethyl-1,2,3-trisilacyclopentane is similar to that of compound 3. This compound is photolyzed to give dimethylsilylene and polymeric substances. Again, the four-membered ring compound, 1,2-disilacyclobutane, is never detected.

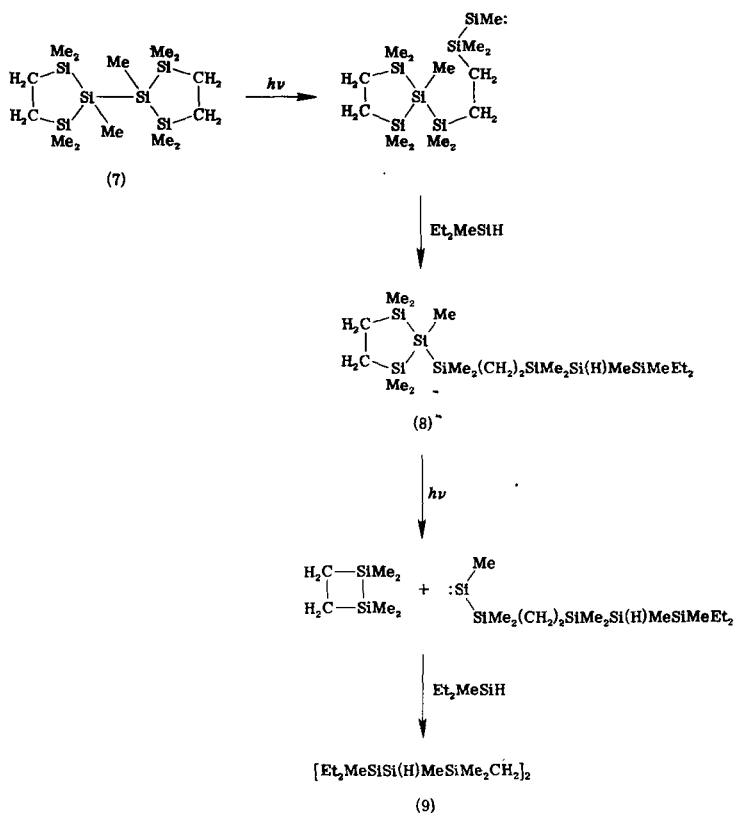


Photolysis of silyl-substituted polysilacycloalkanes is of considerable interest (39). When 2,3-bis(trimethylsilyl)-1,1,2,3,4,4-hexamethyl-1,2,3,4-tetrasilacyclohexane (**4**) is photolyzed in the presence of diethylmethylsilane, 2-trimethylsilyl-1,1,2,3,3-pentamethyl-1,2,3-trisilacyclopentane (**5**) and silylene insertion product **2** are obtained in 47 and 50% yield, respectively. However, photolysis of compound **5** (or prolonged irradiation of **4**) in the presence of the same quencher leads to an unexpected compound identified as 2,2,3,3,6,6,7,8-octamethyl-8-ethyl-2,3,6,7,8-pentasiladecane (**6**) in 22% yield, in addition to 60% yield of compound **2**. The formation of compounds **2** and **6** indicates that the photochemical degradation of **5** proceeds simultaneously by two different pathways giving two types of silylene species as shown in Scheme 3. Once again, no 1,2-disilacyclobutane is obtained.

On the other hand, the photolysis of bis(1,1,2,3,3-pentamethyl-1,2,3-trisilacyclopentyl) (**7**) under the same photolysis conditions as above reveals that the silylene species is expelled in a different manner in two distinct steps. In contrast to **5**, the photolysis of **7** proceeds to give only one kind of silylene species in each step. In the first step, compound **8**, to be expected from the insertion of the silylene generated by a 1,2-shift of a trisilacyclopentane ring into diethylmethylsilane, is formed. In the second step, compound **8** thus formed undergoes further photolysis yielding an-



SCHEME 3

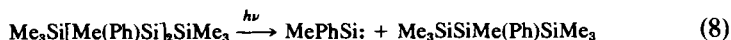


SCHEME 4

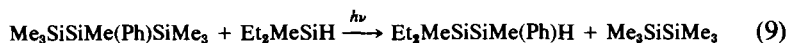
other type of the silylene which can readily insert into a Si—H bond to give compound **9**, as shown in Scheme 4.

D. Phenyl-Substituted Polysilanes

The photolysis of phenyl-substituted polysilanes also affords a convenient method for generation of silylene species. Irradiation of 2,3-diphenyloctamethyltetrasilane in a hexane solution produces methylphenylsilylene and 2-phenylheptamethyltrisilane which undergoes further photolysis yielding the same silylene and hexamethyldisilane (**40**, **41**).



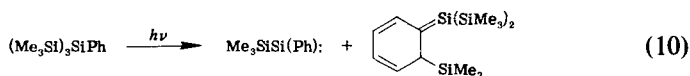
When a hexane solution of 2-phenylheptamethyltrisilane is photolyzed in the presence of a large excess of diethylmethylsilane by irradiation with a low-pressure mercury lamp, 1,1-diethyl-1,2-dimethyl-2-phenyldisilane is obtained in 47% yield as the sole insertion product (42). The absence of



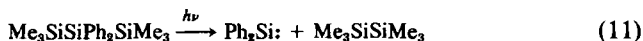
homo-coupling products such as 1,2-dimethyl-1,2-diphenyldisilane, expected if the silylene abstracted hydrogen and underwent radical coupling, suggests that the methylphenylsilylene is present in a singlet state electronic configuration.

The stereochemistry of photochemical generation of dimethylsilylene has been reported (43). Photolysis of *cis*- and *trans*-1,2,2,3-tetramethyl-1,3-diphenyl-1,2,3-trisilacycloheptane in hexane with a low-pressure mercury lamp proceeds in a highly stereospecific manner with retention of configuration at both Si-1 and Si-3 centers.

The photolysis of tris(trimethylsilyl)phenylsilane results in formation of trimethylsilylphenylsilylene in high yield, together with a small amount of a silicon-carbon double-bonded intermediate, which will be described in detail later. This silylene has a high reactivity toward unsaturated organic substrates such as alkenes and alkynes (44).



Similar photolysis of 2,2-diphenylhexamethyltrisilane by irradiation with a high-pressure mercury lamp yields diphenylsilylene and hexamethyldisilane (45).



III

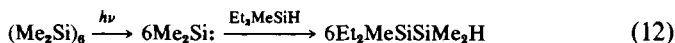
REACTIONS OF PHOTOCHEMICALLY GENERATED SILYLENES

Photochemically generated silylene species may react either with themselves to form polysilane polymers, or with a trapping agent added to intercept the species. The fate of the silylene and the structure of reaction products depend on the relative rates of these two processes, which may proceed simultaneously.

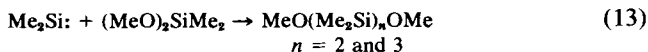
A. Insertion into Single Bonds

A wide variety of reactions that involve the insertion of thermally generated inorganic and organic silylenes into a heteropolar single bond has been reported (3). However, the reaction of photochemically generated silylenes with compounds having such a bond has not been extensively investigated. A few examples involving the insertion into Si—H, Si—O, Si—Cl, and H—Cl bonds are known.

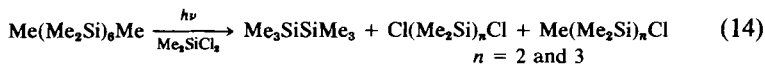
As already described, hydrosilanes are one of the most suitable silylene trapping agents and are often used in photolysis. Thus, the photolysis of dodecamethylcyclohexasilane in diethylmethylsilane affords the insertion product in 46% yield, on the basis of the following stoichiometric equation (31).



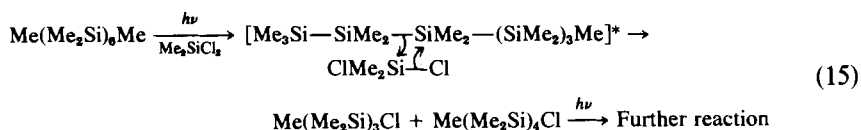
The insertion of thermally generated inorganic and organic silylenes into silicon–oxygen or silicon–halogen bonds in polysilanes is quite general (3). However, several attempts to effect related reactions with monosilane derivatives have been unsuccessful. For examples, silicon tetrafluoride does not react with difluorosilylene (46, 47), and the reaction of dimethylsilylene with dimethyldimethoxysilane has been shown to be kinetically unimportant in the thermolysis of 1,2-dimethoxytetramethyldisilane (48). However, the insertion of dimethylsilylene generated by photolysis of dodecamethylcyclohexasilane into the silicon–oxygen bond of dimethoxydimethylsilane proceeds smoothly to give, in high yield, 1,2-dimethoxytetramethyldisilane and 1,3-dimethoxyhexamethyltrisilane in the ratio of 1.6:1 (31).



The photolysis of tetradecamethylhexasilane in dimethyldichlorosilane gives rise to unexpected results; hexamethyldisilane, dichlorotetramethyldisilane, dichlorohexamethyltrisilane, chloropentamethyldisilane, and 1-chloroheptamethyltrisilane are formed in the ratio of 1.0:1.6:2.6:2.0:1.3, respectively.



This unusual feature of the photolysis in dimethyldichlorosilane indicates that a direct reaction of photochemically excited polysilanes with the chlorosilane to give monochloropolysilanes occurs in competition with the generation of dimethylsilylene (31).



Photolysis of dodecamethylcyclohexasilane in cyclohexane under bubbling dry hydrogen chloride gas admixed with nitrogen carrier gives dimethylchlorosilane in 72% yield. Polydimethylsilane, obtained from sodium-condensation of dimethyldichlorosilane in boiling toluene, also reacts with hydrogen chloride under the same photolysis conditions when suspended in cyclohexane to give dimethylchlorosilane (49). These reac-



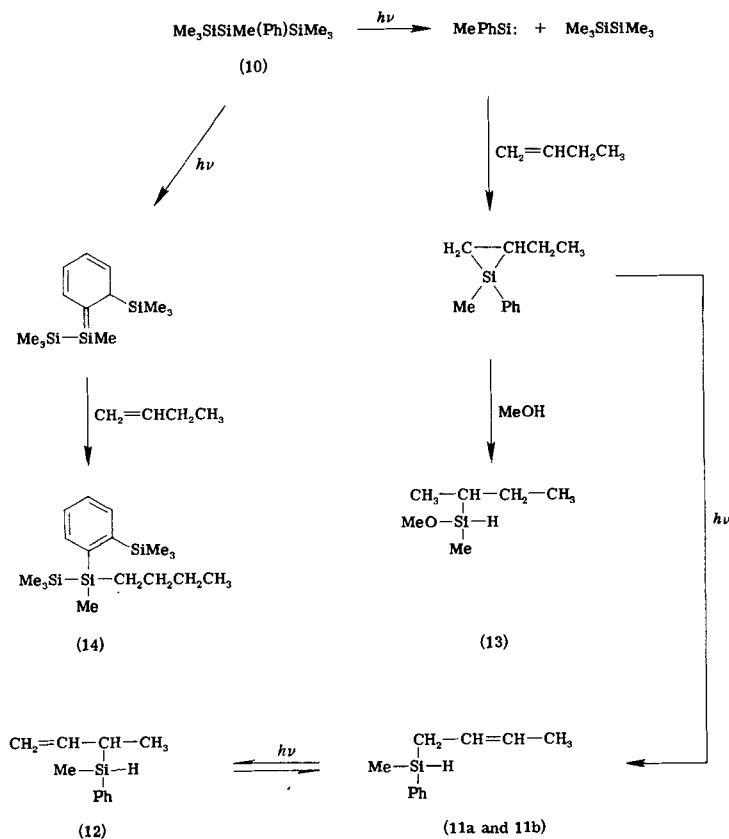
tions may involve both the insertion of dimethylsilylene into the H—Cl bond and the direct reaction of photoexcited polysilanes with hydrogen chloride.

B. Addition to Alkenes

Methylphenylsilylene generated photochemically from 2-phenylheptamethyltrisilane (**10**) adds readily to the carbon-carbon double bonds of many types of olefin (50–52). Interestingly, when a high-pressure mercury lamp with a quartz filter is used for the generation of the silylene, a methylphenylsilyl-substituted alkene arising from photochemical isomerization of the silacyclopropane is obtained, very often as the main product. However, when a low-pressure mercury lamp is used, a silacyclopropane which can readily be transformed into the methoxysilane by treating the photolysis mixture with methanol is produced, together with a trace of the silyl-substituted alkene. Thus, photolysis of a hexane solution of **10** with a high-pressure mercury lamp in the presence of 1-butene affords *cis*- and *trans*-1-methylphenylsilyl-2-butene (**11a** and **11b**) and 3-methylphenylsilyl-1-butene (**12**) in 17, 6, and 4% yields, respectively, in addition to a small amount of product **14** arising from the reaction of a silicon-carbon double-bonded intermediate with 1-butene (*vide infra*), as shown in Scheme 5 (52). As will be discussed later, the formation of **11a** and **11b** can be accounted for by the photorearrangement of a 1-silacyclopropane intermediate involving a 1,3-hydrogen shift from carbon to the ring silicon atom. Indeed, treatment of the reaction mixture produced from the photol-

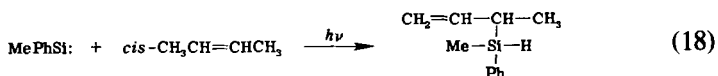
ysis experiments with methanol after the irradiation is stopped gives a low yield of methoxysilane (13) arising from the methanolysis of the 1-silacyclopropane. Careful product analysis in the early stages of the reaction indicates that 3-methylphenylsilyl-1-butene (12) is not an initial product, but is produced in the photoisomerization of 11a and 11b. Similar photolysis of 10 with a high-pressure mercury lamp in the presence of a terminal olefin such as 1-octene, isobutene, isopropenyltrimethylsilane, or allyltrimethylsilane gives the respective methylphenylsilyl-substituted alkenes (20–39% yield) analogous to 11 (52).

Internal olefins and cyclic olefins also react with methylphenylsilylene to give silyl-substituted olefins. Irradiation of 10 with a high-pressure mercury lamp in the presence of *cis*-2-butene in hexene yields 3-methylphenylsilyl-1-butene in 29% yield. Small amounts of the photoisomer 1-methyl-

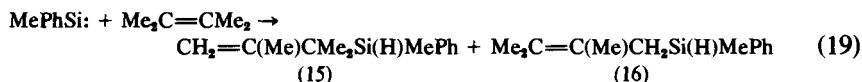


SCHEME 5

phenylsilyl-2-butene are also produced. In this reaction, however, the addition of methanol to the product mixture does not produce any methoxysilanes, indicating that complete photoisomerization of the silacyclopropane to the silylalkene takes place during the photolysis.

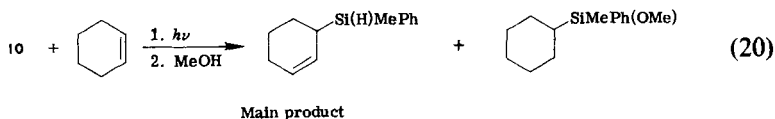


The reaction of methylphenylsilylene with tetramethylethylene under similar photolysis conditions gives two compounds, 2,3-dimethyl-3-methylphenylsilyl-1-butene (**15**) and an isomer, 2,3-dimethyl-1-methylphenylsilyl-2-butene (**16**), in 20 and 11% yield, respectively.

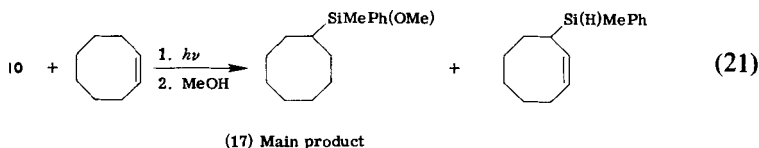


The irradiation of either pure **15** or **16** with a high-pressure mercury lamp in hexane gives an equilibrium mixture consisting of **15** and **16** in a ratio of 51:49, showing that **16** comes from photoisomerization of **15** via a 1,3-silyl shift.

Photolysis of **10** in the presence of cyclohexene followed by methanolysis affords 3-(methylphenylsilyl)cyclohexene and cyclohexylmethylphenylmethoxysilane in 27 and 7% yield, respectively.



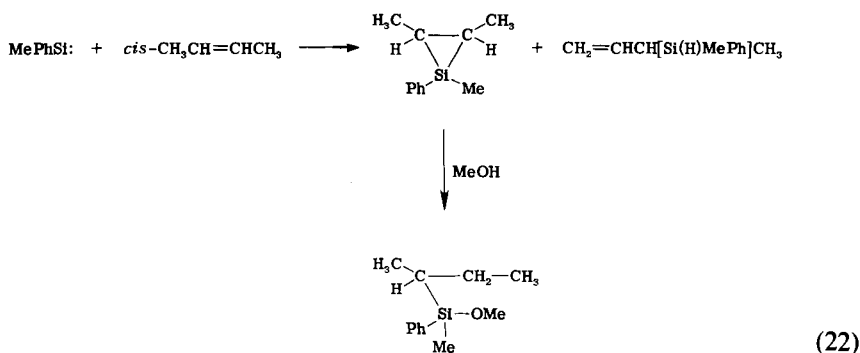
In contrast to the above results, irradiation of **10** with cyclooctene followed by methanolysis gives cyclooctylmethylphenylmethoxysilane (**17**) in 34% yield, and photoisomer 3-(methylphenylsilyl)cyclooctene in only 4% yield.



If a low-pressure mercury lamp with a Vycor filter is used for the photolysis of **10** in the presence of olefins, silacyclopropanes are obtained (52,

53). Under this photolysis condition, the rates of photoisomerization of the initially formed silacyclopropanes to the silylalkenes are rather slow. Irradiation of a hexane solution of **10** in the presence of 1-butene followed by treatment of the photolysis mixture with dry methanol after irradiation was stopped, affords 2-(methylphenylmethoxysilyl)butane in 27% yield, along with a small amount of silylalkenes. Similar photolysis of **10** in the presence of internal olefins or cyclic olefins gives the respective silacyclopropanes as the main products, together with the photorearranged silylalkenes as minor ones. These silacyclopropanes cannot be isolated by distillation or by GLC because of their extreme kinetic instability, but the formation of the silacyclopropanes can be determined by proton NMR spectroscopy (52).

The yields of the silacyclopropanes are highly dependent on the structure of the olefins used. In general, substrates bearing one or two methyl groups on an olefinic carbon atom afford appreciable amounts of photorearranged silylalkenes and low yields of silacyclopropanes. Thus, the photolysis of **10** in the presence of *cis*-2-butene in hexane using a low-pressure mercury lamp, followed by methanolysis, gives 2-methoxymethylphenylsilylbutane in 26% yield and the silylalkene in 10% yield. With isobutene as substrate, *tert*-butylmethoxymethylphenylsilane and 2-methyl-3-methylphenylsilylpropene are obtained in 18 and 22% yield, re-



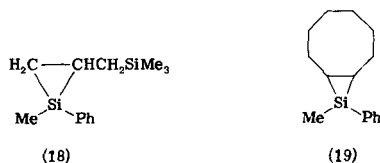
spectively. When tetramethylethylene is used as a quencher, only a trace of the methoxysilane is obtained along with small amounts of the silylalkenes.



Irradiation of **10** in the presence of olefins that do not have methyl groups on an olefinic carbon atom, such as 1-butene, 1-octene, allyltimethylsi-

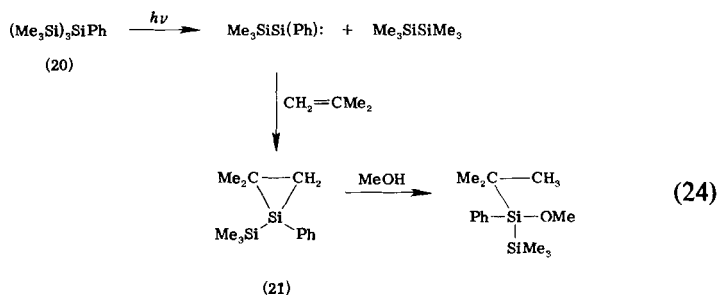
lane, cyclohexene, and cyclooctene, produces the respective silacyclopropanes in moderate yield (27–50%), and only small amounts of the silylalkenes (3–4%) are formed. That the ratio of the silacyclopropane to the silylalkene does not depend on the reaction temperature is confirmed by the fact that low-temperature photolysis of **10** in the presence of isobutene affords the same result as room temperature photolysis.

All of the silacyclopropanes investigated to date with the exception of **18** and **19** undergo photorearrangement to give silylalkenes in high yields, when irradiated with a high-pressure mercury lamp with a quartz filter. Photochemical degradation of **18** and **19** proceeds by two different routes.



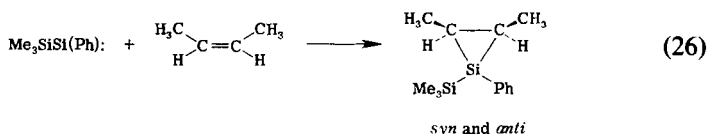
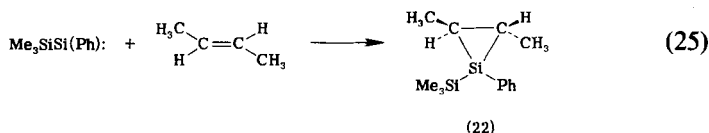
One involves photorearrangement giving the silylalkene mentioned above and the other, the main route, is silylene extrusion, the reverse of the reaction that leads to silacyclopropane formation (52).

Photochemically generated trimethylsilylphenylsilylene also adds to the carbon–carbon double bonds of many types of olefins (54). Thus, the photolysis of a hexane solution of tris(trimethylsilyl)phenylsilane (**20**) in the presence of isobutene by irradiation with a low-pressure mercury lamp produces, after subsequent treatment of the photolysis mixture with methanol, *tert*-butylphenyl(trimethylsilyl)methoxysilane in 52% yield, as the sole insertion product. Direct evidence for the formation of 1-trimethylsilyl-1-phenyl-2,2-dimethyl-1-silacyclopropane in this photolysis can be obtained by NMR spectroscopic analysis of the reaction mixture.

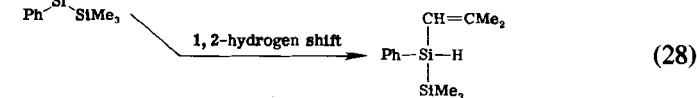
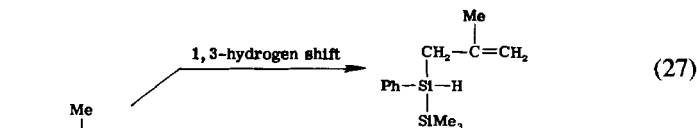


The addition of trimethylsilylphenylsilylene to the olefin proceeds with high stereoselectivity to give the silacyclopropane. Thus, irradiation of

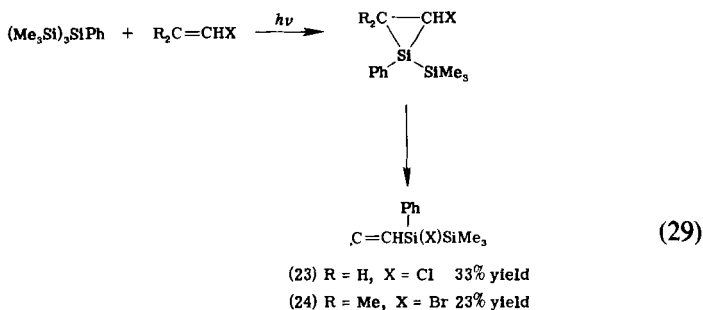
20 with a low-pressure mercury lamp in the presence of *trans*-2-butene affords *trans*-1-trimethylsilyl-1-phenyl-2,3-dimethyl-1-silacyclopropane (**22**) which can be distilled under reduced pressure without decomposition. No other isomer is detected by either GLC or spectroscopic analysis. With *cis*-2-butene, trimethylsilylphenylsilylene reacts to give two stereoisomers, *syn*- and *anti*-silacyclopropane.



The photolysis of silacyclopropanes **21** and **22** by irradiation with a high-pressure mercury lamp proceeds simultaneously by two different routes, one leading to the formation of a 1-alkenyl substituted silane via a 1,2-hydrogen shift which has never been observed in the photolysis of the silacyclopropanes produced from methylphenylsilylene with olefins, and the other involving the usual 1,3-hydrogen shift. The photochemical reaction of **21** is shown in Eqs. (27) and (28) as a typical example.

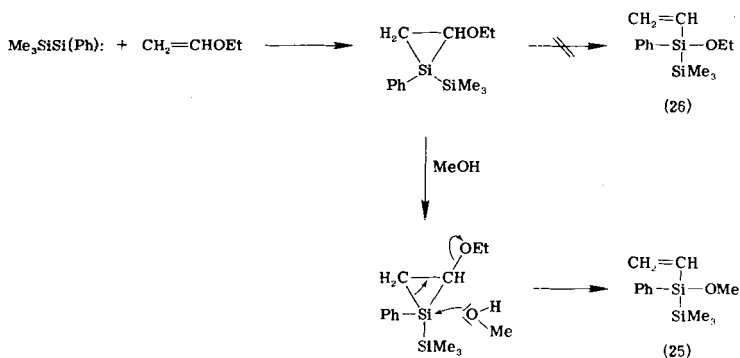


The photolysis of $(\text{Me}_3\text{Si})_3\text{SiPh}$ in the presence of functional substituted olefins is of considerable interest (55). Irradiation of **20** with a low-pressure mercury lamp in the presence of vinyl chloride or 1-bromo-2-methylpropene affords the respective 1-alkenyl-1-halo-1-phenyltrimethyldisilanes as the sole volatile product. The fact that the reaction of trimethylsilylphenylsilylene with butyl bromide does not give any volatile products suggests that compound **23** and **24** must come from a 1,2-halogen shift of



2-chloro- or 2-bromo-1-silacyclopropane produced transiently, and not from direct insertion of trimethylsilylphenylsilylene into the carbon–chlorine or carbon–bromine bond.

Interestingly, photolysis of **20** in the presence of ethyl vinyl ether leads to a different result from that described above. Thus, irradiation of **20** with an excess of ethyl vinyl ether in hexane produces an unstable product that is never detected by GLC. However, addition of dry methanol to this solution at room temperature immediately affords 1-methoxy-1-phenyl-1-vinyltrimethyldisilane (**25**) in 17% yield. No 1-ethoxy-1-phenyl-1-vinyltrimethyldisilane (**26**) is observed in this reaction. The fact that the methoxy/ethoxy exchange reaction between ethoxysilane **26**, prepared by independent route, and methanol under identical conditions proved to be slow enough to be followed by GLC, indicates that methoxysilane **25** must be produced by the reaction of initially formed 1-trimethylsilyl-1-phenyl-2-ethoxy-1-silacyclopropane with methanol. A possible mechanism for the formation of **25** involving a nucleophilic attack of methanol on the silicon atom in the silacyclopropane ring, followed by elimination of the ethoxy group from the ring carbon atom, is shown in Scheme 6.

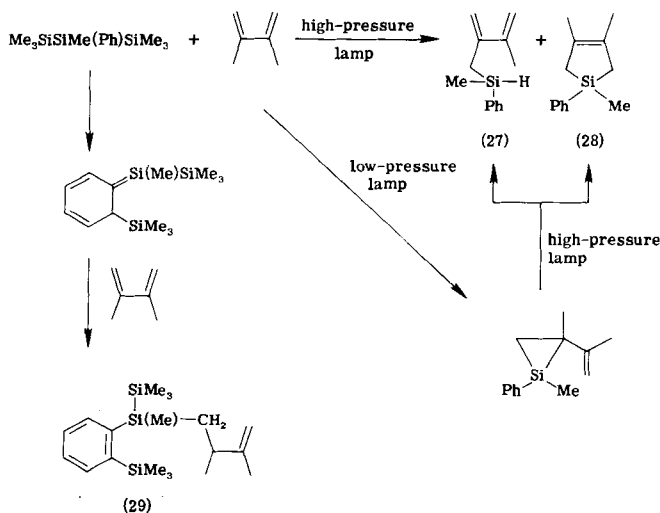


SCHEME 6

C. Addition to Dienes

Most of the reactions of the thermally generated silylenes with acyclic 1,3-dienes lead to silacyclopent-3-enes. These apparent 1,4-addition products have been assumed to form from a 1,2-addition of the silylenes to the dienes, followed by rearrangement (56–58), although the corresponding alkenylsilacyclopropanes are never detected by either GLC or spectroscopic analysis. In contrast to the thermally generated silylenes, photochemically generated methylphenylsilylene reacts with 1,3-butadiene derivatives to give products arising from the 1,2-adducts, together with the apparent 1,4-adducts. Irradiation of $\text{Me}_3\text{SiSiMe(Ph)SiMe}_3$ with a high-pressure mercury lamp in the presence of 2,3-dimethylbutadiene, isoprene, or 1,3-butadiene in a hexane solution gives the respective 2-methylphenylsilylmethyl-substituted 1,3-butadienes, in addition to 1-silacyclopentene derivatives. Similar photolysis of **10** with a low-pressure mercury lamp affords alkenylsilacyclopropanes which can be quenched by methanol to the methoxysilanes, along with the silyl-substituted 1,3-butadienes and the silacyclopentenenes (59, 60).

Irradiation of **10** in the presence of 2,3-dimethylbutadiene with a high-pressure mercury lamp produces 2-(methylphenylsilylmethyl)-3-methyl-1,3-butadiene (**27**) and 1,3,4-trimethyl-1-phenyl-1-silacyclopentene (**28**) in 11 and 18% yield, respectively. The rearranged addition product (**29**) of **10** and 2,3-dimethylbutadiene is also obtained in 16% yield. Similar photolysis of a hexane solution of **10** using a low-pressure mercury lamp af-



SCHEME 7

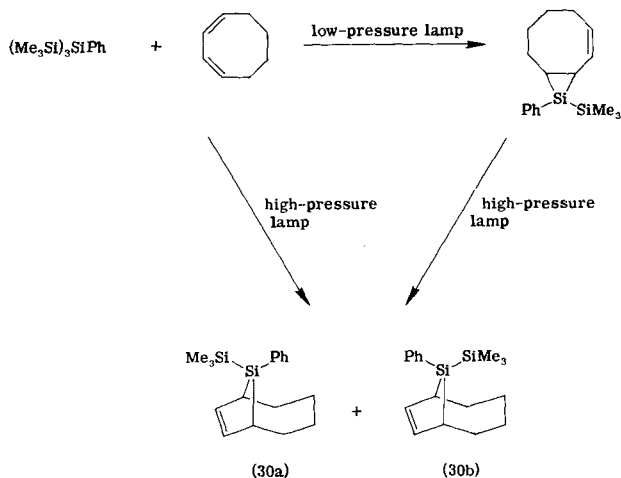
fords the alkenylsilacyclopropane, quenched with methanol as 2-(methoxymethylphenylsilylmethyl)-3-methyl-2-butene in 10% yield, in addition to **27** (8% yield), **28** (13% yield), and **29** (25% yield) (Scheme 7). Irradiation of the solution involving the alkenylsilacyclopropane with a high-pressure mercury lamp leads to complete transformation of the silacyclopropane into **27** and **28**. In this photolysis, **27** and **28** are obtained in 25 and 32% yield, respectively, on the basis of the silacyclopropane. Photochemically generated trimethylsilylphenylsilylene also reacts with a conjugated diene to give the 1,2-adduct which can be quenched by methanol (**54**).

Interestingly, irradiation of **20** with a low-pressure mercury lamp in the presence of 1,3-cyclooctadiene yields 9-phenyl-9-trimethylsilyl-9-silabicyclo[6.1.0]nona-2-ene as the sole silylen $\dot{\text{e}}$ insertion product. This compound readily isomerizes to give two isomers of 9-phenyl-9-trimethylsilyl-9-silabicyclo[4.2.1]nona-7-ene (**30a** and **30b**) when irradiated with a high-pressure mercury lamp. On the other hand, similar photolysis of **20** using a high-pressure mercury lamp affords 9-silabicyclo[4.2.1]nona-7-enes, **30a** and **30b**, as the sole volatile products as shown in Scheme 8 (**54**).

These results clearly indicate that the insertion of silylene species into conjugated dienes proceeds via a 1,2-addition followed by rearrangement to the silacyclopentene.

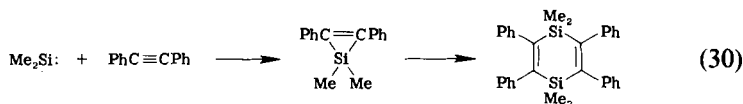
D. Addition to Alkynes

In 1961, Vol'pin *et al.* (**61**, **62**) reported the isolation of a compound with an empirical formula $\text{C}_{16}\text{H}_{18}\text{Si}$ from reaction of dimethylsilylene with



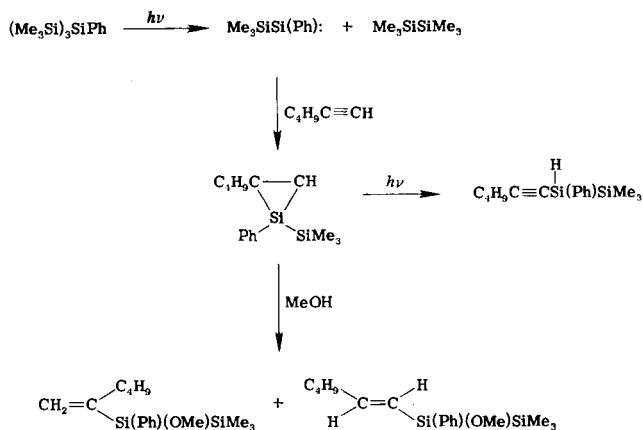
SCHEME 8

diphenylacetylene, which they supposed to have the novel silacyclopropene structure. However, the proposed structure was soon discovered to be incorrect, with the actual product being the 1,4-disilacyclohexa-2,5-diene (63–65). Since that time, considerable interest has been shown in



the possible existence of the silacyclopropenes. Recently, Conlin and Gaspar (66) have reported that dimethylsilylene generated by thermolysis of 1,2-dimethoxytetramethyldisilane reacts with 2-butyne to give tetramethyl-1-silacyclopropene. More recently, Seyferth and his co-workers (67) have reported the isolation of 1,1-dimethyl-2,3-bis(trimethylsilyl)-1-silacyclopropene which is formed by thermolysis of hexamethylsilirane in the presence of bis(trimethylsilyl)acetylene.

In contrast, photochemically generated dimethylsilylene and methylphenylsilylene do not react with acetylenes. However, trimethylsilylphenylsilylene has been found to add to the triple bond of various alkynes, giving the silacyclopropene derivatives (68, 69). The silacyclopropenes from monosubstituted alkynes are thermally unstable. Therefore GLC techniques cannot be used for determining directly the yields of the silacyclopropenes produced in the photochemical reactions. For the purpose of estimating the yield, methanolysis is used. Irradiation of **20** with a low-pressure mercury lamp in the presence of 1-hexyne in hexane produces 1-phenyl-1-trimethylsilyl-2-butyl-1-silacyclopropene. Treatment of this solution with methanol after irradiation was stopped affords the two methoxysilanes to be expected from methanolysis of the silacyclopropene, 2-(1'-methoxy-1'-phenyltrimethyldisilanyl)-1-hexene and (*E*)-1-(1'-methoxy-1'-phenyltrimethyldisilanyl)-1-hexene in 21 and 4% yield, respectively. In this photolysis, 1-(1'-phenyl-2',2',2'-trimethyldisilanyl)hexyne derived from the photochemical isomerization of the silacyclopropene, via a 1,2-hydrogen shift, is also obtained in 14% yield (Scheme 9). No other volatile products such as 1,4-disilacyclohexa-2,5-diene are observed by GLC or spectroscopic analysis. Careful analysis of the reaction products during the photolysis indicates that the silacyclopropene is the only product in the early stages of the reaction; no 1-(1'-phenyl-2',2',2'-trimethyldisilanyl)hexyne can be observed. Photolysis of **20** with trimethylsilylacetylene similarly produces the rearranged product, trimethylsilyl(1'-phenyl-2',2',2'-trimethyldisilanyl)acetylene in 40% yield, in addition to 16% yield (as methoxysilane) of 1,2-bis(trimethyl-

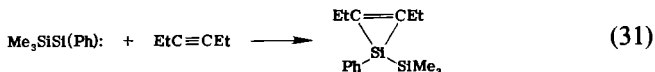


SCHEME 9

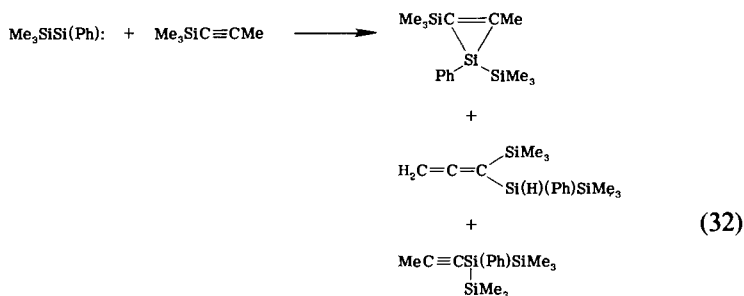
silyl)-2-phenyl-1-silacyclopropene. Formation of silyl-substituted alkynes from the reaction of the thermally generated silylene with acetylene and propyne has also been reported (70, 71).

Trimethylsilylphenylsilylene also reacts with disubstituted acetylenes such as 3-hexyne, 1-trimethylsilylpropyne, bis(trimethylsilyl)acetylene, and 2,2,5,5-tetramethyl-3-hexyne to give the respective silacyclopropenes. The silacyclopropenes thus formed, with the exception of 1,2,3-tris(trimethylsilyl)-1-phenyl-1-silacyclopropene, can be distilled under reduced pressure without decomposition.

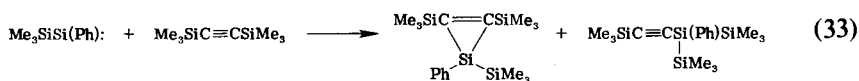
Photolysis of a hexane solution of **20** in the presence of 3-hexyne gives 1-trimethylsilyl-1-phenyl-2,3-diethyl-1-silacyclopropene which can be isolated in pure form by distillation followed by preparative GLC.



Similar photolysis of **20** in the presence of 1-trimethylsilylpropyne produces a silacyclopropene in 33% yield. In this case, small amounts of two other compounds, 1-trimethylsilyl-1-(1'-phenyl-2',2',2'-trimethyldisilyl)propadiene (2% yield) arising from a 1,3-hydrogen shift of the initially formed silacyclopropene and 1-bis(trimethylsilyl)phenylsilylpropyne (2% yield), are also obtained. Formation of the latter compound can be best explained in terms of another type of photochemical migration in-



volving a 1,2-trimethylsilyl shift from carbon to the silicon atom in the three-membered ring. A photochemical 1,2-silyl shift is also observed in the photolysis of **20** in the presence of bis(trimethylsilyl)acetylene. In this photolysis, 1,2,3-tris(trimethylsilyl)-1-phenyl-1-silacyclopropene and [bis(trimethylsilyl)phenylsilyl]trimethylsilylacetylene are obtained in 24 and 9% yield, respectively. The fact that the ratio of the silacyclopropene to the silylalkyne does not change in the low-temperature photolysis at



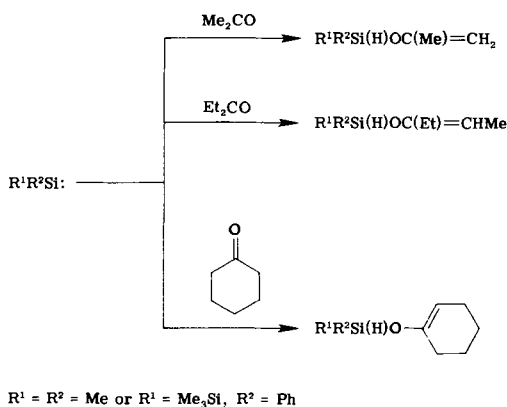
–78°C indicates that the silylalkyne must be produced by a photochemical process under the conditions used.

1-Trimethylsilyl-1-phenyl-2,3-di-*tert*-butyl-1-silacyclopropene obtained from the photolysis of **20** in the presence of di-*tert*-butylacetylene in 33% yield, is kinetically rather stable. When a hexane solution of this silacyclopropene is exposed to air for 5 min, 30% of the silacyclopropene is recovered unchanged. Such anomalous behavior may be attributed to the presence of the bulky substituents on the carbon atoms in the silacyclopropene ring (69).



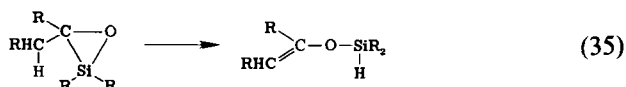
E. Addition to Carbonyl Compounds

Photochemically generated silylenes react with enolizable ketones to give silyl enol ethers. Irradiation of **20** with a low-pressure mercury lamp in the presence of acetone, diethyl ketone, or cyclohexanone gives the re-

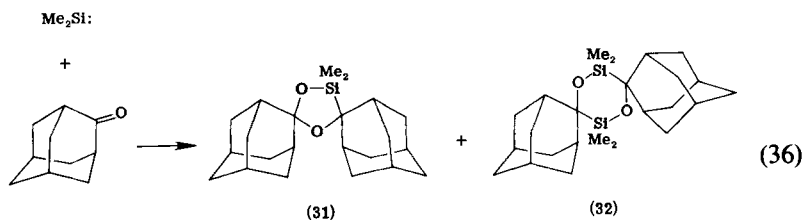


SCHEME 10

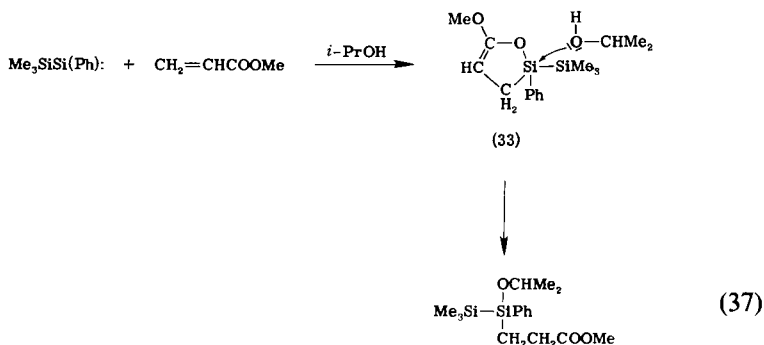
spective 1-phenyl-2,2,2-trimethyldisilanyl enol ethers (72) as shown in Scheme 10. Dimethylsilylene generated photochemically from $(Me_2Si)_6$ has



also been found to react with the carbonyl compounds yielding the silyl enol ethers (73). The silyl enol ethers might be produced by the reaction of the silylenes with enol forms of the ketones, but the concentrations of enol forms are very small under the conditions used. A more probable mechanism involves initial formation of an oxasilacyclopropane, followed by isomerization to the observed products. Indeed, dimethylsilylene generated by photolysis of $(Me_2Si)_6$ reacts with the nonenolizable ketone 2-adamantanone to give two compounds, **31** and **32**, as the main products, indicating the transient formation of oxasilacyclopropane (74).



Irradiation of **20** with methyl acrylate in hexane and treatment of the photolysis product with isopropyl alcohol yields methyl 3-(1'-isopro-



poxy-1'-phenyltrimethyldisilanyl)propionate (24% yield) whose formation can be explained by the reaction of **33** with isopropyl alcohol (72).

IV

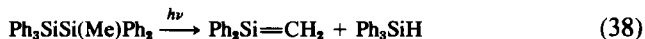
SILICON-CARBON DOUBLE-BONDED INTERMEDIATES

In 1967, Gusel'nikov and Flowers (75) reported that gas-phase pyrolysis of 1,1-dimethylsilacyclobutene generates dimethylsilaethene, $\text{Me}_2\text{Si}=\text{CH}_2$, which, in the absence of trapping agent, dimerizes to give 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Evidence for the transient formation of this unsaturated silicon compound has been shown by kinetic studies and also by trapping technique (76). Since then, many papers concerning the formation and reactions of the thermally generated silaethenes have been published (77).

Photochemical formation of silaethene intermediates has also been reported (27, 78-82). However, little systematic study had been done until 1975 when we initiated a series of studies on the photolysis of aryl-, alkenyl-, and alkynyl-substituted disilanes.

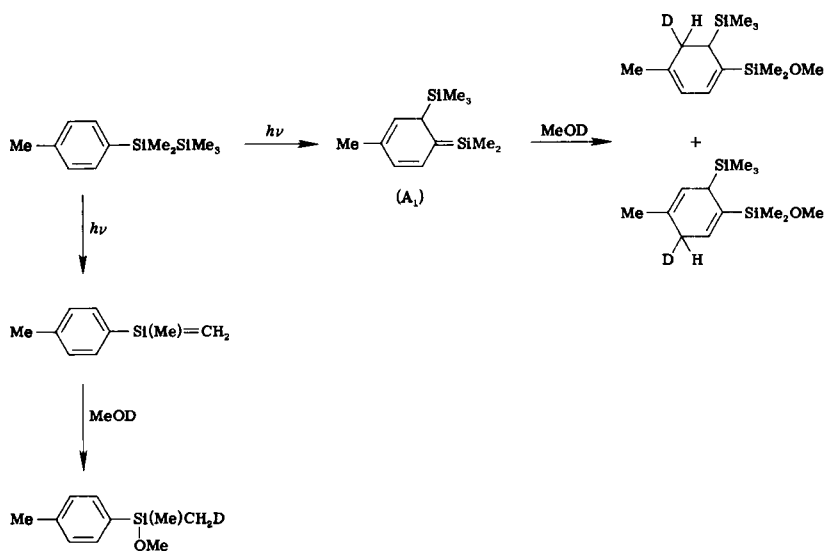
A. Photolysis of Benzenoid Aromatic Derivatives of Disilanes

In 1972, Sommer and co-workers (78) reported the first example of a silicon-carbon double bonded intermediate generated by the photolysis of pentaphenylmethyldisilane.



In 1975, we discovered that photolysis of arylidisilanes produces a novel type of the silicon-carbon double-bonded intermediate (83). The structure of this intermediate is quite different from that of the diphenylsilaethene reported by Sommer *et al.* A transient formation of the reactive intermediate can be confirmed by trapping experiments. Thus, the photolysis of *p*-tolylpentamethyldisilane with a low-pressure mercury lamp in the presence of methanol- d_1 affords 1,4- and 1,6-adducts, 1-methoxydimethylsilyl-4-methyl-5-deutero-6-trimethylsilyl-1,3-cyclohexadiene, and 1-methoxydimethylsilyl-3-deutero-4-methyl-6-trimethylsilyl-1,4-cyclohexadiene in 27 and 28% yield (Scheme 11). In this photolysis, monodeutero methoxydimethylsilyltoluene to be expected from the reaction of the silaethene intermediate, *p*-CH₃C₆H₄Si(Me)=CH₂, with methanol- d_1 produces in only 2% yield (84).

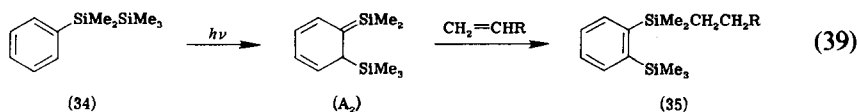
The photochemical generation of the silicon-carbon double-bonded intermediate from the benzenoid aromatic derivatives of disilane is a quite general and remarkably clean reaction. All of such arylidisilanes bearing a hydrogen atom on the ortho carbon in the benzene ring, for instance, phenyl-substituted disilanes, Ph_{*n*}Si₂Me_{*n-6*} with *n* = 1–5, and tolyl and anisylpentamethyldisilanes are readily photolyzed on irradiation with a low-pressure mercury lamp in hexane or in benzene to give the respective silicon-carbon double-bonded intermediates analogous to A₁ (85, 86). The



SCHEME 11

intermediates thus formed are thought to polymerize in the absence of a trapping agent. No products that might be expected from dimerization of the intermediates have been observed. The intermediates, however, react readily with trapping agents such as alkenes, dienes, alkynes, and carbonyl compounds in a different fashion than do the silaethene intermediates.

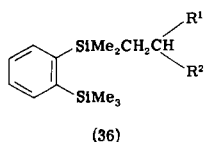
The photolysis of phenylpentamethyldisilane (**34**) in the presence of ethylene or any of its monosubstituted derivatives always gives the respective 1:1 adducts in moderate yields (83, 87).



R = H, Et, C₃H₁₁, OEt, Ph, SiMe₃

Interestingly, in these reactions a stoichiometric amount of the olefin can trap the intermediate A₂ as effectively as an excess amount. For instance, irradiation of a benzene solution of **34** with a 20-fold excess of vinyltrimethylsilane affords **35** (R = Me₃Si) in 37% yield. Under identical conditions **34** reacts with a one molar equivalent of vinyltrimethylsilane to give **35** (R = Me₃Si) in 41% yield. This indicates that the intermediate A has a lifetime long enough to allow it to find a partner in a dilute solution.

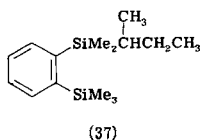
With A₂ in benzene, 1,1-disubstituted olefins generally afford better yields of the adducts than do monosubstituted olefins. However, with olefins having an electron-withdrawing substituent such as CN or COOMe, yields of the adducts are lower. Thus, photolysis of **34** in the presence of one molar equivalent of methacrylonitrile gives **36** [(R¹ = Me, R² = CN)



in 15% yield as the sole volatile product. Introduction of an electron-donating group such as Me₃SiO onto the unsaturated carbon atom does not greatly change the yield (35%) of **36** (R¹ = Me, R² = Me₃SiO). The reaction of A₂ with olefins such as 1,1-dimethyl-, 1,1-bis(trimethylsilyl)-, 1-methyl-1-phenyl-, and 1-phenyl-1-trimethylsilylethene gives good yields (46–56%) of **36**.

The photolysis of **34** in the presence of internal olefins is of interest be-

cause the yield of adducts depends highly on the structure of olefins used in a different sense than do the yields from terminal olefins. The addition of intermediate A to the *cis* olefins affords always better yields of the adducts than those from the *trans* isomers (87). For example, irradiation of **34** with *cis*-2-butene produces adduct **37** in 32% yield as the sole volatile product. On the other hand, with *trans*-2-butene under identical conditions, the intermediate A_2 reacts to give **37** in only 17% yield. No other volatile product is detected by GLC analysis. The proton NMR spectrum of polymeric substances from the photolysis product shows that they con-



tain no alkyl moiety arising from 2-butene. These results indicate that a model for the addition step which involves "end-on" approach of olefin to the intermediate from the side trans to the Me_3Si group in the cyclohexadienyl ring as shown in Fig. 2 would be ruled out, because there is no appreciable difference in steric interaction for both olefin isomers. On the other hand, models in which an olefin molecule approaches the intermediate A "side-on" seem to account for the observed results. Examination of molecular models shown that a *trans* isomer of olefin experiences a significant steric interaction as compared with the *cis* isomer (Fig. 3).

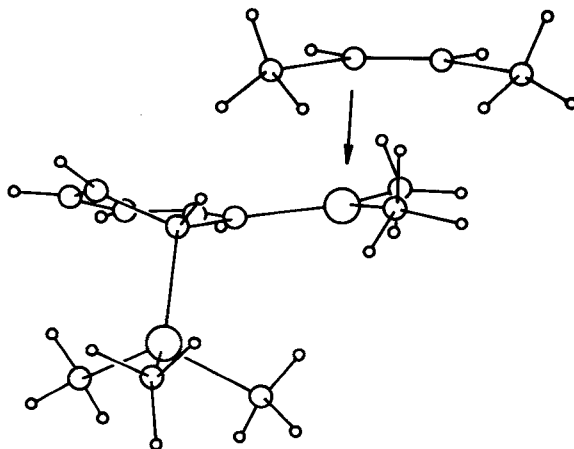


FIG. 2. Schematic representation of "end-on" approach of olefin to intermediate A_2 .

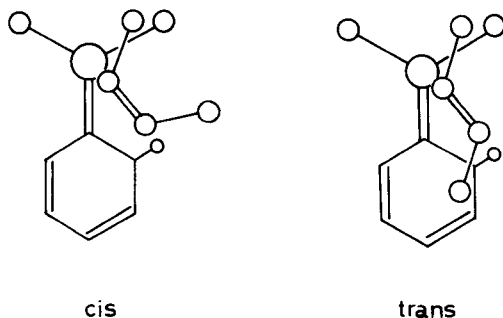
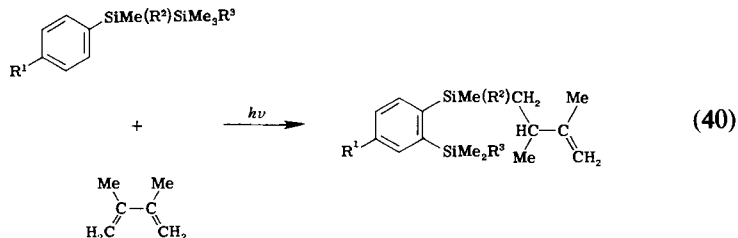


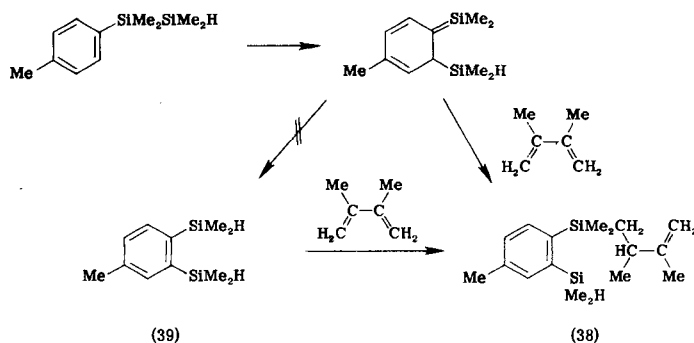
FIG. 3. Schematic representation of "side-on" approaches of olefin to intermediate A_2 .

When vinylsilanes such as dimethylvinyl-, trimethylvinyl-, and ethyldimethylvinylsilane are used as trapping agents in the photolysis of $\text{PhMe}_2\text{SiSiMe}_3$ silepin derivatives are always formed in 5–9% yield, in addition to the normal adducts (88).

Irradiation of aryldisilanes with 2,3-dimethylbutadiene in benzene affords adducts whose structures are similar to the structure of **35** (85). In no case are [2 + 2]- or [2 + 4]-cycloaddition products formed.



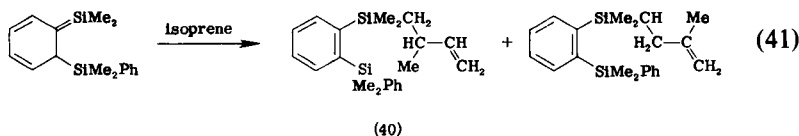
These results sharply contrast with those observed in the reaction of thermally generated silaethene-type intermediates with conjugated dienes, where [2 + 4]-cycloaddition takes place to give the corresponding 1-silacyclohex-3-ene (77). Interestingly, the photolysis of phenyl- and tolyl-substituted disilanes bearing a silicon–hydrogen bond in the presence of 2,3-dimethylbutadiene under similar conditions gave analogous results to those of the phenyl- and tolylpentamethyldisilane systems. No hydrodisilanylation products which might be derived from the reaction of the starting arylhydrodisilanes with the diene are observed. In particular, it should be noted that the photolysis of $p\text{-MeC}_6\text{H}_4\text{SiMe}_2\text{SiMe}_2\text{H}$ in the presence of 2,3-dimethylbutadiene gives only **38** as a product. This fact demonstrates amply that the reaction does not involve the hydrosilane **39**



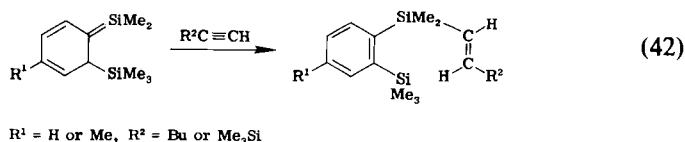
SCHEME 12

expected from an intramolecular shift in the silicon-carbon double-bonded intermediate (Scheme 12).

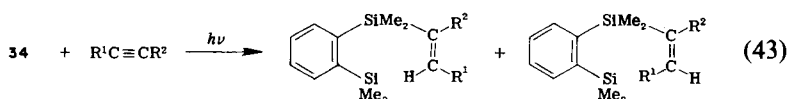
1,3-Butadiene and isoprene also react with the intermediates to give the expected adducts. With isoprene, two possible isomers are obtained in the ratio of 2.3:1. The abundant isomer in this reaction is **40**, produced from addition of the reactive intermediate across the carbon-carbon double bond bearing the methyl group.



Similar irradiation of **34** and *p*-tolylpentamethyldisilane with 1-hexyne or trimethylsilylacetylene in benzene leads to the formation of (*E*)-olefins in moderate yields (89). In no case are (*Z*)-isomers detected. The quenching capacity of the acetylenic compounds, however, seems lower than

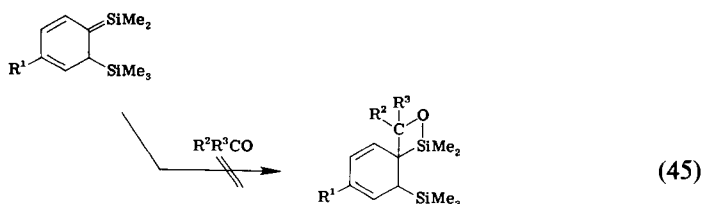
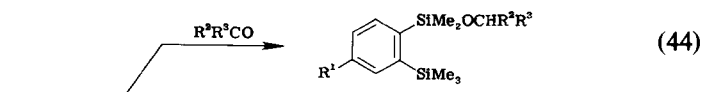


that of olefins or dienes which produce the adducts in higher yields. Irradiation of **34** with bis(trimethylsilyl)acetylene under similar conditions affords both (*E*)- and (*Z*)-olefins in the ratio of 56:44. Similar photolysis of **34** in the presence of phenylacetylene in benzene gives also (*E*)- and (*Z*)-



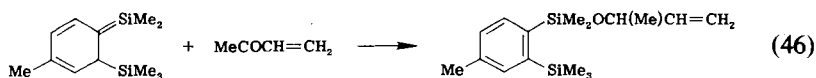
olefins in the ratio of 52:48. Control experiments indicate that both (*E*)- and (*Z*)-isomers are produced as initial products of the photolysis. Acetylene also reacts with the intermediates of type A at room temperature to give the corresponding adducts as the sole volatile products but in low yields.

In marked contrast to the reaction of the silaethene intermediates, $R_2Si=CH_2$, with ketones at high temperature (90, 91), the reaction of all the silicon-carbon double-bonded intermediates generated from the arylpentamethyldisilanes with either enolizable or nonenolizable ketones yields 2-trimethylsilyl(alkoxydimethylsilyl)benzene derivatives (92). Neither silyl enol ethers to be expected from O—H addition of enol form of enolizable ketones to the silicon-carbon double bond nor products from a

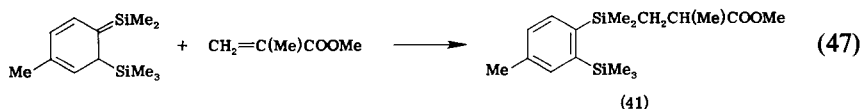


pseudo-Wittig reaction are observed. These results are consistent with the fact that the reaction of the intermediate A with methanol affords no 1,2-adduct.

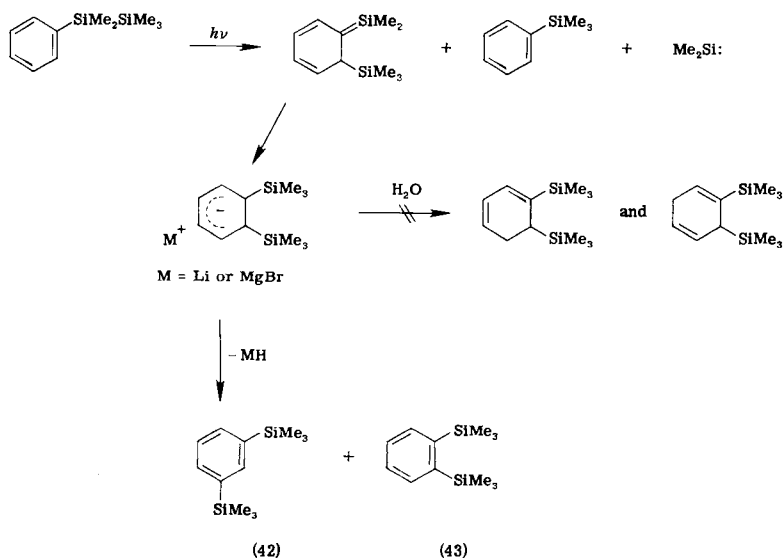
Intermediate A reacts with conjugated carbonyl compounds to give 1:1 adducts (92). Reaction of the intermediate produced from *p*-tolylpentamethyldisilane with methyl vinyl ketone affords 2-trimethylsilyl-4-methyl(methylallyloxydimethylsilyl)benzene in 51% yield as the sole volatile product. Acrolein also reacts with phenylpentamethyldisilane under similar photolysis conditions to give 2-trimethylsilyl-4-methyl(allyloxydi-



methylsilyl)benzene in 40% yield. The photolysis of *p*-tolylpentamethyldisilane in the presence of methyl methacrylate proceeds in a different manner to give a product **41** that results from addition of the intermediate to the carbon–carbon double bond, but not to the carbon–oxygen double bond (92).



The reaction of the silicon–carbon double-bonded intermediate generated from phenylpentamethyldisilane with methyllithium and with methylmagnesium bromide leads to the formation of wholly unexpected products (93). Thus, irradiation of **34** in the presence of methyllithium with a low-pressure mercury lamp in diethyl ether followed by hydrolysis produces 1,3-bis(trimethylsilyl)benzene (**42**) and 1,2-bis(trimethylsilyl)benzene (**43**) in 60 and 20% yield, respectively, in addition to an 8% yield of phenyltrimethylsilane (Scheme 13). Surprisingly, no disilyl-substituted cyclohexadienes that might be expected from addition of methyllithium to the intermediate followed by hydrolysis are observed. In this photolysis,



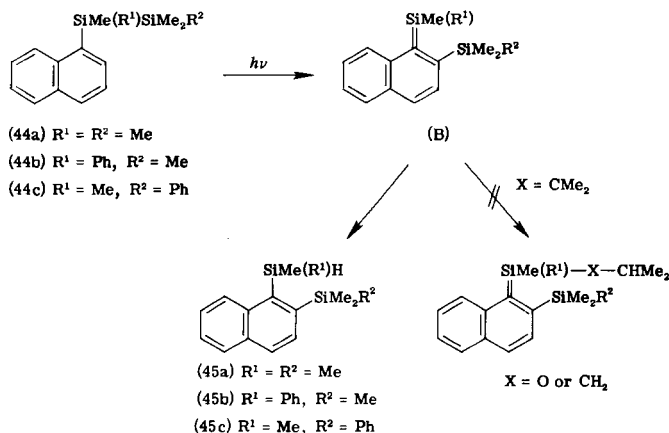
SCHEME 13

both the yield and the product ratio depend on the solvent used. Irradiation of **34** with methyllithium in tetrahydrofuran under similar photolysis conditions followed by treatment with water affords **43** and phenyltrimethylsilane in 9 and 2% yield, along with approximately 1% yield of **42**. In dioxane, however, results similar to those in diethyl ether are obtained.

Photolysis of **34** in the presence of methylmagnesium bromide in tetrahydrofuran gives **42** in 38% yield, in addition to a 2% yield of phenyltrimethylsilane. In this case, a trace of **43** is produced. In diethyl ether, intermediate **A** reacts with methylmagnesium bromide to give **42** and **43** in 12 and 14% yield, while in dioxane, **42** and **43** are formed in 2 and 25% yield, respectively. On the other hand, photolysis of **43** in the presence of methyllithium in diethyl ether under the same photolysis conditions as above, followed by hydrolysis, gives no isomerization product **42**, indicating that the production of **42** must involve an anionic rearrangement of the trimethylsilyl group from the ortho- to the meta-carbon atom in the organometallic intermediate prior to elimination of the metal hydride, while the metal hydride elimination from the initially formed addition product would lead to the formation of **43**. The production of phenyltrimethylsilane can be explained in terms of a photochemical 1,2-phenyl migration with simultaneous generation of dimethylsilylene during photolysis of **34** (84, 94).

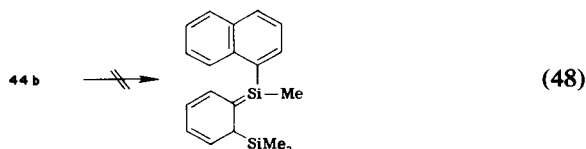
B. Photolysis of Naphthyldisilanes

Both 1-disilanyl- and 2-disilanylnaphthalenes undergo photolysis upon irradiation with a low-pressure mercury lamp, yielding the respective silicon-carbon double-bonded intermediates (95). However, the chemical behavior of the two types of the intermediates is different in many respects. In contrast to the photolysis of benzenoid aryldisilanes, which produce reactive intermediates **A** readily adding to many types of substrate as described above, the reactive intermediate from 1-pentamethyldisilanylnaphthalene (**44a**) never added to these substrates. An isomer, 1-dimethylsilyl-2-trimethylsilylnaphthalene (**45a**) is always obtained. Thus, when a solution of **44a** in benzene containing isobutene is irradiated with a low-pressure mercury lamp, a 40% yield of **45a** is obtained as the sole volatile product (Scheme 14). No 1-isobutyldimethylsilyl-2-trimethylsilylnaphthalene, which might be expected to arise from addition of silicon-carbon double-bonded intermediate to isobutene, is detected. Similar photolysis of **44a** in the presence of acetone and of methanol affords isomer **45a** in 62 and 66% yield, respectively. Interestingly, irradiation of **44a** in the absence of the trapping agent again affords **45a** in 64% yield. The



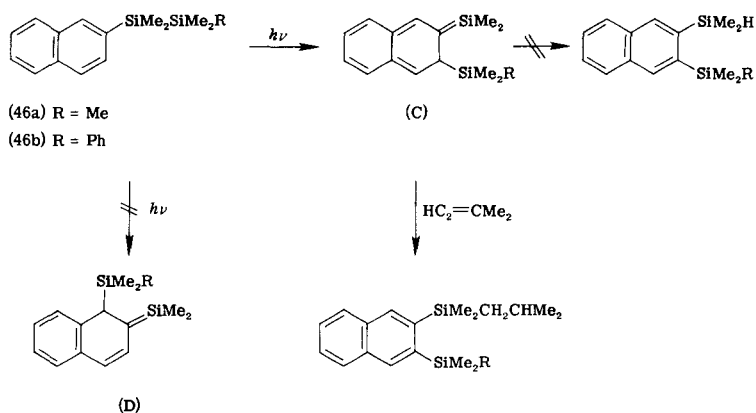
SCHEME 14

production of **45a** which can be explained by an intramolecular hydrogen shift in intermediate B is of considerable interest, because silicon-carbon double-bonded intermediates of type A do not afford any volatile products in the absence of a trapping agent. Such isomerization involving a rapid 1,3-hydrogen shift in intermediate B is a remarkably general reaction for 1-disilanyl-substituted naphthalenes. Thus, irradiation of 1-(1'-phenyltetramethyldisilanyl)naphthalene (**44b**) in the presence of acetone produces **45b** in 61% yield. In this case, the migration of the trimethylsilyl group occurs exclusively to the naphthalene ring but not to the benzene ring. Similar irradiation of **44c** in the absence of a quencher gives 1-dimethylsilyl-2-dimethylphenylsilylnaphthalene (**45c**) in 29% yield. In this case, however, 1-phenyldimethylsilylnaphthalene arising from an intra-



molecular 1,2-naphthyl shift from one silicon atom to the other is also obtained in 22% yield.

Unlike the 1-disilanyl-substituted naphthalenes, photolysis of 2-disilanyl naphthalenes (**46**) gives intermediate C, which readily adds to the substrate present (95). Thus, irradiation of **46a** in the presence of isobutene in benzene affords an adduct, 2-isobutyldimethylsilyl-3-trimethylsilyl naphthalene in 37% yield, as the sole volatile product. Interestingly, pho-



SCHEME 15

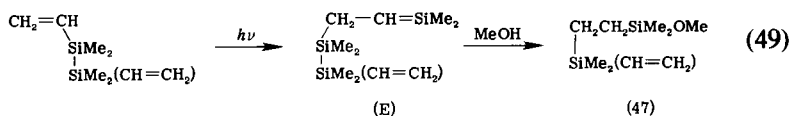
tolysis of **46a** in the absence of quenchers does not produce any volatile products such as 2-dimethylsilyl-3-trimethylsilylnaphthalene but affords polymeric substances (Scheme 15). Similar irradiation of **46b** with isobutene produces again the 2,3-bis(silyl)-substituted naphthalene as the sole volatile product. Neither the 1,2-isomer that might be expected from the reaction of intermediate D with isobutene nor the 1,2-bis(silyl)-substituted benzene is detected.

On the basis of the results of CNDO/2 calculations and the concept of orbital interaction, the intermediate B is expected to be in an excited state; but the intermediate C and the intermediates from benzenoid disilanes are thought to be in the ground state. This may account for the anomalous chemical behavior of intermediate B (95).

C. Photolysis of α -Alkenyldisilanes

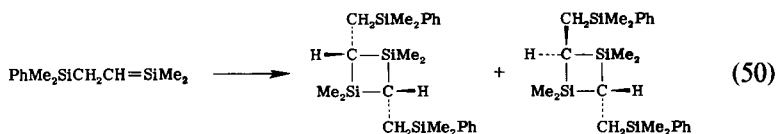
The silicon-carbon double-bonded intermediates of type A generated photochemically from aryldisilanes are appreciably different from thermally generated silaethenes in their mode of reaction with alkenes, conjugated dienes, alkynes, and carbonyl compounds as described earlier. Reasons for the different chemical behavior are probably not due to the difference in methods of generation but largely to the following facts: a great tendency of the intermediates A to stabilize themselves by restoring the aromatic sextet via addition to an unsaturated substrate with a simultaneous hydrogen shift from ring to the substrate and the presence of a bulky substituent, such as a trimethylsilyl group, adjacent to the silicon-

carbon double bond in the intermediate A. Indeed, the chemical behavior of silicon-carbon double-bonded intermediates generated by photolysis of α -alkenyldisilane derivatives is similar to that of the thermally generated silaethenes. Irradiation of 1,2-divinyltetramethyldisilane with a low-pressure mercury lamp in benzene leads to the formation of intermediate E by photorearrangement of a dimethylvinylsilyl group to the terminal carbon of a vinyl group. Intermediate E can be trapped by methanol leading to **47** in 72% yield (96). Similar photolysis of 1-phenyl-2-vinyltetra-



methyldisilane, 1-phenyl-1-vinyltetramethyldisilane, and α -styrylpentamethyldisilane produces the respective silicon-carbon double bonded intermediates analogous to intermediate E (97, 98). Irradiation of 1-phenyl-2-vinyltetramethyldisilane, which contains both phenylsilicon and vinylsilicon groupings, in the presence of methanol produces only 1-methoxydimethylsilyl-2-phenyldimethylsilylethane (82% yield), indicating that migration of a silyl group occurs exclusively to the vinylic carbon atom. Similarly, 1-phenyl-1-vinyltetramethyldisilane is converted on photolysis in the presence of methanol to 1-methoxymethylphenylsilyl-2-trimethylsilylethane in good yield. Again, no product arising from a 1,3-shift of the silyl group to the phenyl ring followed by methanol is detected.

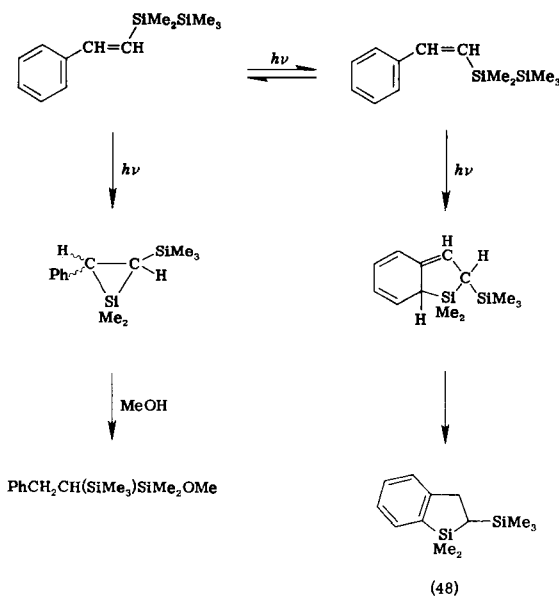
In sharp contrast to the silicon-carbon double-bonded intermediates of type A, which never afford any volatile products in the absence of a suitable substrate, intermediates of type E may undergo dimerization to give a head-to-tail dimer. Thus, when a solution of 1-phenyl-2-vinyltetramethyldisilane in dry hexane is photolyzed, *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-bis(dimethylphenylsilylmethyl)-1,3-disilacyclobutane can be obtained in 21 and 22% yield, respectively.



The photolysis of (*E*)-2-phenylethenylpentamethyldisilane gives wholly unexpected results. Thus, irradiation of a benzene solution of (*E*)-Ph-CH=CH-SiMe₂SiMe₃ in the presence of methanol for 1 h affords an equilibrium mixture consisting of (*E*)- and (*Z*)-isomers in the ratio of

1.3:1. In this case, no product arising from the reaction of the silicon-carbon double-bonded intermediate with methanol can be observed at all. However, on prolonged irradiation of the solution two products, 1,1-dimethyl-2,3-benzo-5-trimethylsilyl-1-silacyclopentene (**48**) and 1-methoxydimethylsilyl-1-trimethylsilyl-2-phenylethane are obtained in 17 and 7% yield, in addition to the (*Z*)- and (*E*)-isomers (15 and 12% yield). The formation of the latter compound can best be understood by the transient formation of a silacyclopropane followed by reaction with methanol (*98*). The mechanism for the production of **48** in the prolonged irradiation of $\text{PhCH}=\text{CHSiMe}_2\text{SiMe}_3$ is not fully understood but is tentatively given in Scheme 16.

The silicon-carbon double-bonded intermediates generated photochemically from α -alkenyldisilane derivatives react with both enolizable and nonenolizable ketones to give olefins (*98*). For instance, the photolysis of α -styrylpentamethyldisilane (**49**) in the presence of one molar equivalent of acetone gives 1-trimethylsilyl-2-phenyl-3-methyl-2-butene in 13% yield as a single product. No silyl enol ether to be expected from the reaction of the intermediate with the enol form of acetone is observed. Similar irradiation of **49** with acetophenone affords (*E*)- and (*Z*)-1-trimeth-



SCHEME 16

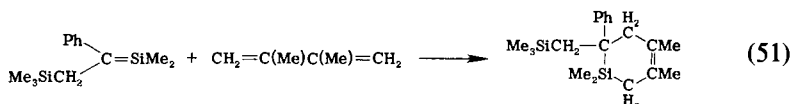


Irradiation of **49** with methyl vinyl ketone under similar conditions produces two types of compounds, (*E*)- and (*Z*)-3-methyl-4-phenyl-5-trimethylsilyl-1,3-pentadiene and 2,6,6-trimethyl-5-trimethylsilylmethyl-5-phenyl-1-oxa-6-silacyclohexene-2, in 7, 7, and 18% yield, respectively



(Scheme 18). The 1,3-pentadiene derivatives may be formed by an initial [2 + 2]-cycloaddition reaction, while the formation of the 1-oxa-6-silacyclohexene derivative can be explained by a direct [2 + 4]-cycloaddition reaction (98). It has been reported that the reaction of thermally generated silaethene derivatives with acrolein affords products that can be accounted for in terms of initial competing [2 + 2]- and [2 + 4]-cycloaddition reaction between the intermediates and acrolein (99).

On the other hand, photolysis of **49** in the presence of 2,3-dimethylbutadiene gives a [2 + 4]-cycloaddition product as the sole volatile product. No [2 + 2]-cycloaddition product is detected by GLC and spectroscopic analysis.

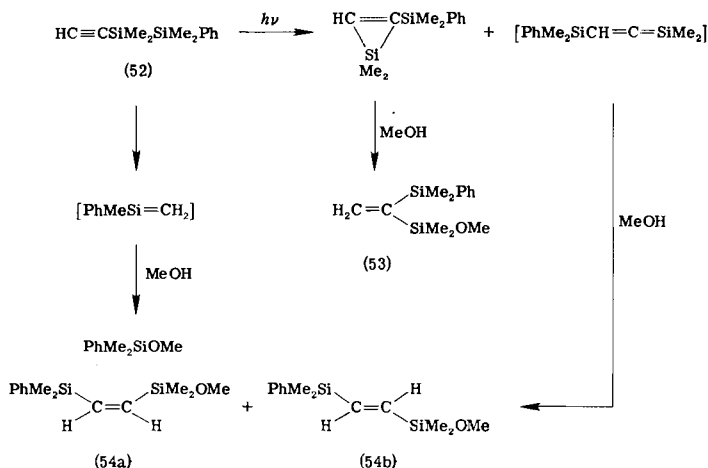


V

PHOTOLYSIS OF ALKYNYLDISILANES

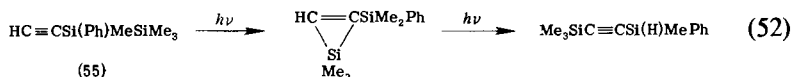
The photochemical behavior of alkynyldisilanes is quite different from that of the alkenyldisilanes (100). The photolysis of 1-ethynyl-2-phenyltetramethyldisilane (**52**) with a low-pressure mercury lamp leads to simultaneous production of three different types of intermediate, silacyclopentene, silapropadiene, and silaethene, which react readily with methanol to give the respective methoxysilanes. Thus, irradiation of **52** in the presence of methanol in hexane affords four products, 1-methoxydimethylsilyl-1-dimethylphenylsilylethene (**53**), *cis*- and *trans*-1-methoxydimethylsilyl-2-dimethylphenylsilylethene (**54a** and **54b**), and methoxydimethylphenylsilane, in 11, 10, 6, and 30% yield, respectively, with 84% conversion of the starting **52** as shown in Scheme 19. Irradiation of **52** in the absence of methanol under similar conditions, followed by treatment of the resulting mixture with methanol without irradiation, affords only nonvolatile substances. No methoxysilane **53** arising from the silacyclopentene is detected.

Irradiation of 1-ethynyl-1-phenyltetramethyldisilane (**55**) leads to the formation of the silacyclopentene and silapropadiene which can be trapped by methanol to give 1-trimethylsilyl-1-methoxymethylphenylsilylethene (29% yield) and *cis*- and *trans*-1-trimethylsilyl-2-methoxymethylphenylsilylethene (19 and 15% yield). In contrast to **52**, the photolysis of

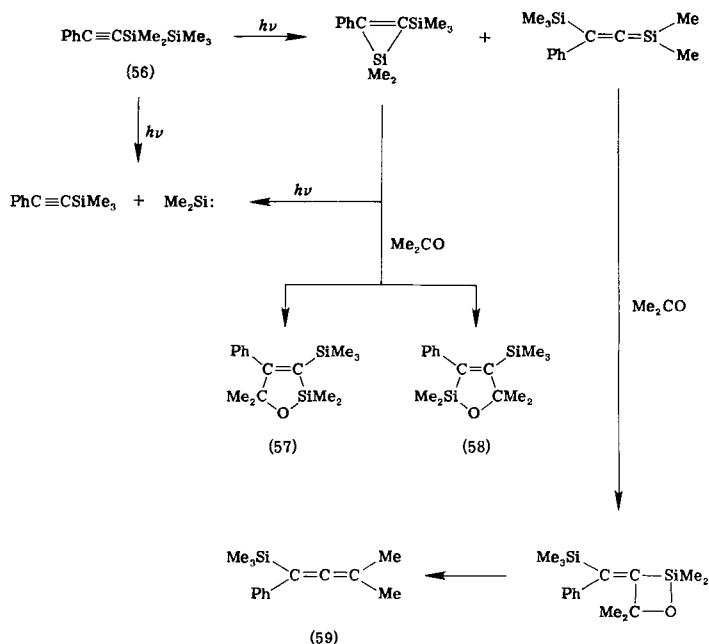


SCHEME 19

55 in the absence of methanol gives trimethylsilyl(methylphenylsilyl)acetylene, to be expected from a 1,2-hydrogen shift of the transiently formed silacyclopentene, in 25% yield as the sole volatile product. In the presence of methanol, methoxysilanes arising from the reaction of both silacyclopentene and silapropadiene with methanol are obtained. The photochemical behavior of $\text{HC} \equiv \text{CSiPh}_2\text{SiMe}_3$ is similar to that of **55**.

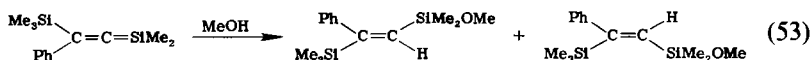


The photolysis of phenylethynylpentamethyldisilane (**56**) takes place simultaneously by at least two different processes. The main route proceeds through a silacyclopentene and the other involves transient formation of a silapropadiene. Irradiation of a benzene solution of **56** in the presence of acetone gives four products, 2,2,5,5-tetramethyl-3-trimethylsilyl-4-phenyl-1-oxa-2-silacyclo-3-pentene (**57**), 2,2,5,5-tetramethyl-3-phenyl-4-trimethylsilyl-1-oxa-2-silacyclo-3-pentene (**58**), phenyltrimethylsilylacetylene, and 1-phenyl-1-trimethylsilyl-3-methyl-1,2-butadiene (**59**), in 51, 2, 10, and 5% yield, respectively, with 81% conversion of the starting disilane. The formation of **57** and **58** can be explained by insertion of acetone into the silacyclopentene. Liberation of dimethylsilylene species from either direct photolysis of **56** or decomposition of the silacyclopentene results in the formation of $\text{PhC} \equiv \text{CSiMe}_3$. Product **59**



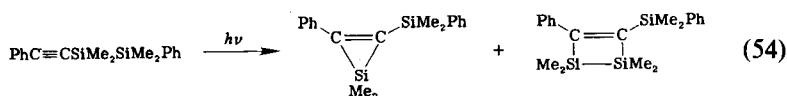
SCHEME 20

can be rationalized in terms of cycloaddition of acetone to the silapropadiene intermediate giving the silaoxetane intermediate, followed by loss of the Me_2SiO moiety, as shown in Scheme 20 (101). The silapropadiene can also be trapped by methanol as (*E*)- and (*Z*)-1-phenyl-1-trimethylsilyl-2-methoxydimethylsilylethylene (101, 102).

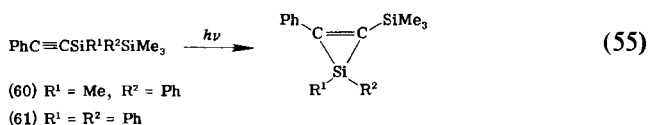


The photolysis of a benzene solution of **56** in the absence of a trapping agent with a low-pressure mercury lamp and distillation of the resulting mixture under reduced pressure affords 1,1-dimethyl-2-phenyl-3-trimethylsilyl-1-silacyclopropene in 41% yield as a colorless liquid, along with 10% yield of trimethylsilylphenylacetylene (103).

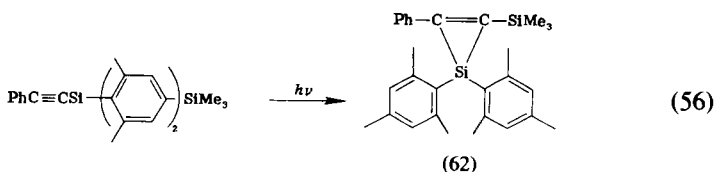
It has been shown that the photolysis of phenylethynyl-substituted disilanes affords a convenient route to the synthesis of the silacyclopropene derivatives (104). For instance, irradiation of 1-phenylethynyl-2-phenyl-tetramethyldisilane with a low-pressure mercury lamp gives 1,1-dimethyl-2-phenyl-3-dimethylphenylsilyl-1-silacyclopropene and 1,1,2,2-tetra-



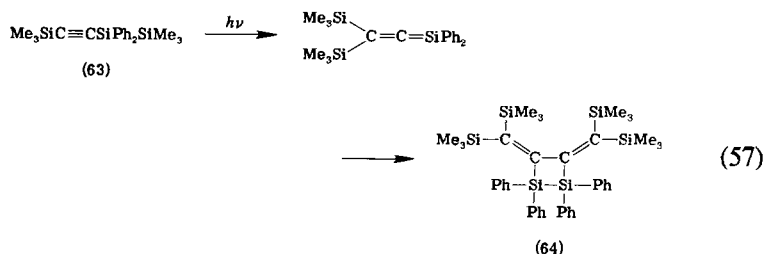
methyl-3-phenyl-4-dimethylphenylsilyl-1,2-disilacyclobut-3-ene in 54 and 2% yield, respectively. Similar photolysis of 1-phenylethynyl-1-phenyl-tetramethyldisilane (**60**) and 1-phenylethynyl-1,1-diphenyltrimethyldisilane (**61**) in a hexane solution produce 1-methyl-1,2-diphenyl-3-trimethylsilyl-1-silacyclopentene and 1,1,2-triphenyl-3-trimethylsilyl-1-silacyclopentene in 67 and 61% yield, respectively. These silacyclopentenes can



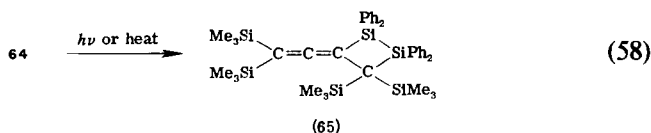
be isolated as colorless liquids by distillation from the photolysis mixture under reduced pressure, followed by preparative GLC. However, they are as extremely air sensitive as the silacyclopentenes reported previously. On exposure to air they decompose readily to give nonvolatile substances (104). In contrast, the silacyclopentene (**62**) produced from photolysis of 1-phenylethynyl-1,1-dimesityltrimethyldisilane in hexane is unaffected by air and moisture. Compound **62** can readily be isolated by preparative TLC under atmospheric oxygen. Neither acetone nor methanol react with **62** in the presence or absence of solvent at room temperature. In all cases, silacyclopentene **62** is recovered quantitatively (105, 106).



The photolysis of 1-trimethylsilylethynyl-1,1-diphenyltrimethyldisilane (**63**) is of considerable interest, because of a novel 1,2-disilacyclobutene is produced (107). When a benzene solution of **63** is photolyzed by irradiation with a low-pressure mercury lamp bearing a Vycor filter, yellow crystals of 1,1,2,2-tetraphenyl-3,4-bis[bis(trimethylsilyl)methylene]-1,2-disilacyclobutane (**64**) are formed. This can be readily isolated by evaporation of the solvent from the resulting mixture. The formation of **64** can be explained in terms of head-to-head dimerization of transiently formed sila-propadiene.

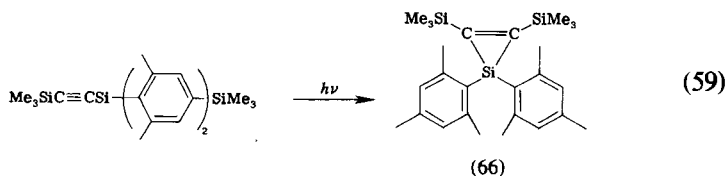


Interestingly, compound **64** undergoes a novel isomerization photochemically or thermally producing another type of 1,2-disilacyclobutane. Thus, irradiation of a benzene solution of **64** with a high-pressure mercury lamp with a Pyrex filter gives colorless crystals (99% yield) identified as 1,1,2,2-tetraphenyl-3-[bis(trimethylsilyl)ethenylidene]-4,4-bis(trimethylsilyl)-1,2-disilacyclobutane. Photochemical and thermal transformation of



64 into **65** can best be explained in terms of 1,3-silyl shift in the disilacyclobutane ring.

The photolysis of 1-trimethylsilylethynyl-1,1-dimesityltrimethylsilane gives a stable crystalline silacyclopentene (**66**) which can be recrystallized from ethanol. Like **62**, this compound is never affected by atmospheric oxygen and moisture (106).



In conclusion, it is fair to say that although the photolysis of a number of organopolysilanes has been investigated recently, work using the reactive species generated photochemically may be developed much further in future years. The photochemical method affords a convenient route to highly strained small compounds such as silacyclopentenes or 1,2-disilacyclobutanes which are otherwise difficult to obtain. Investigation of these compounds may open a new branch of organosilicon chemistry.

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Alkali Metal–Transition Metal π -Complexes

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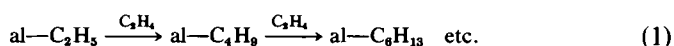
I

INTRODUCTION¹

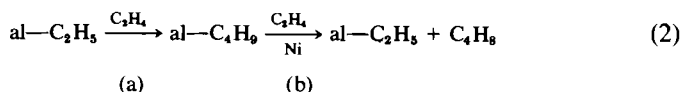
In 1953, Ziegler and Holzkamp (1) observed that the “Aufbaureaktion” (2) of triethylaluminum and ethylene [Eq. (1)] changed to a dimerization of ethylene to butene in the presence of traces of nickel salts [Eq. (2)]. This fundamental discovery, which has become known as the “nickel effect,” led to the development of Ziegler catalysts (3) and was the starting point for the organonickel chemistry of Wilke *et al.* (4, 5).

¹ Abbreviations: acac, acetylacetonate; CDT, cyclododecatriene; COD, cyclooctadiene; Am, alkali metal; Tm, transition metal; THF, tetrahydrofuran; DME, dimethoxyethane; TMEDA, *N,N,N',N'*-tetramethylethylenediamine; Et₂O = diethyl ether.

Insertion reaction ($\text{al} = \frac{1}{3}\text{Al}$):

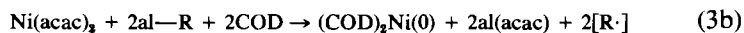
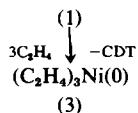


“Nickel effect”:

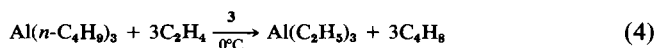


In spite of the many important developments resulting from the nickel effect, little attention has been paid to its mechanism, which is at present considered to consist of an insertion step and a displacement step [Eq. (2a,b)]. Ziegler was the first to discuss the nickel-catalyzed transalkylation [Eq. (2b)] (6). Some time later, Lucas (7) attempted to explain the mechanism of the nickel effect, as did Eisch and Foxton (8), but neither group performed any experiments. Pino *et al.* (9) were the first to attempt to explain the nickel effect on an experimental basis. They found that optical induction resulted in the displacement reaction when using nickel compounds with optically active anions. From this they concluded that at least one of the chiral anions remains bonded to the nickel, i.e., that Ni(I) is involved in the catalytic transalkylation in Eq. (2b). This explanation is not in accord with our findings which have shown that (1) saltlike nickel compounds such as nickel(II) acetylacetonate react even at low temperatures with stoichiometric amounts of AlR_3 , both acetylacetonate groups being exchanged; and that (2) aluminum alkyls still interact with nickel after it has been reduced to Ni(0).

Both of these facts do explain the nickel effect. The first finding is the basis for the syntheses of Wilke's nickel(0)-olefin complexes (1 and 2) [Eq. (3)] (10), while the second reflects the fact that 1, 2, and $(\text{C}_2\text{H}_4)_3\text{Ni}(0)$ (3), which is obtained from 1 and ethylene (11, 12), are highly active catalysts for the transalkylation of aluminum alkyls with olefins as, for example in Eq. (4) (11, 13).



(2)



The nickel(0)-catalyzed transalkylation [Eq. (4)] probably occurs in a complex in which both AlR_3 and olefin are coordinated to the nickel. Presumably, the bond between AlR_3 and nickel is a heterometallic $2e-3c$ bond $\text{R}_2\text{Al}-\text{R}-\text{Ni}(0)$, the olefin being π -bonded to nickel. Both stereochemical and model considerations are in accord with this proposal (13).

This basic concept of the nickel effect is supported by results obtained by means of reactions of nickel complexes 1-3 with more polar organometallics than AlR_3 , i.e., with organo-alkali metal compounds. As shown in Section II, these reactions lead to isolable main-group metal organylnickel(0) π -ligand complexes, some of which have carbanionic organyl groups, that bridge the alkali metal and nickel atoms, e.g., $\text{Am}-\text{R}-\text{Ni}(0)$ groups.

II

ALKALI METAL ORGANYL-, ALKALI METAL HYDRIDO-, AND ALKALI METAL DIORGANYLPHOSPHIDONICKEL(0) π -LIGAND COMPLEXES

A. Classification of Alkali Metal Organylnickel(0) π -Ligand Complexes

If one reacts binary nickel(0)-olefin complexes with organo-alkali metal compounds in the presence or absence of additional molecules capable of functioning as π -ligands but together with n -donor ligands, mixed metal compounds of the type $(\text{AmR})_x(n\text{-donor ligand})_y\text{Ni}(0)(\pi\text{-ligand})_z$ are formed containing either one AmR per Ni or two or three AmR per Ni . Hence, one can differentiate between the complexes of type A ($\text{AmR}/\text{Ni} = 1$), which are ionic, and the nonsaltlike complexes B ($\text{AmC}_6\text{H}_5/\text{Ni} = 2$ or 3). Characteristic of the latter compounds are phenyl groups bridging nickel and alkali metal atoms and bonding between cationic alkali metal atoms and nickel π -ligands (14).

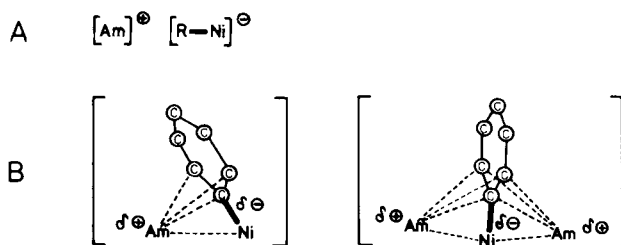
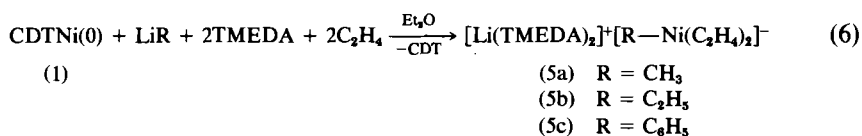
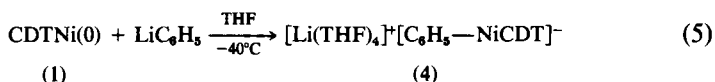


FIG. 1

B. Saltlike Alkali Metal Organylnickel(0)–Olefin Complexes and Saltlike AmH- and AmPR₂Ni(0)–Olefin Complexes

Representative examples of complexes of type A are [Li(THF)₄]⁺[C₆H₅–NiCDT][–] (**4**) (*14*), which is formed from CDTNi(0) (**1**) and phenyllithium in THF, and the complexes (**5**) obtained from **1** or (COD)₂Ni(0) (**2**), LiR, ethylene, and TMEDA (*15*).



The X-ray structure of **5a** is depicted in Fig. 2 (*14*, *15*).

Complex **5a** is composed of separated [Li(TMEDA)₂]⁺ cations and [CH₃–Ni(C₂H₄)₂][–] anions in the crystalline state. The four C atoms of the two ethylene molecules together with the C atom of the methyl group,

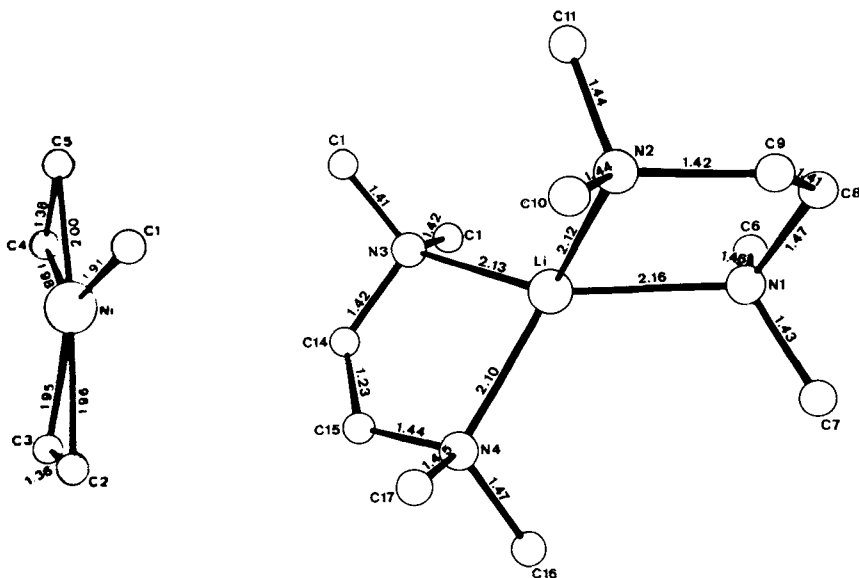


FIG. 2. Molecular structure of [Li(TMEDA)₂]⁺[CH₃–Ni(C₂H₄)₂][–] (**5a**).

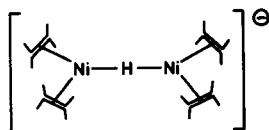
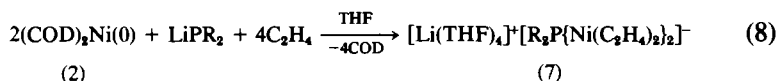
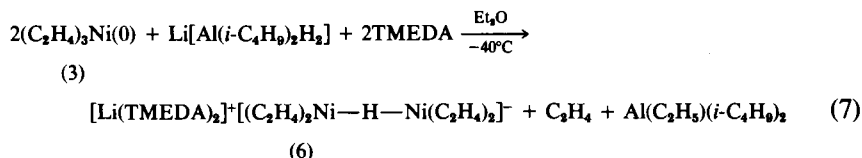


FIG. 3. Proposed structure for the binuclear anion of $[\text{Li}(\text{TMEDA})_2]^+[(\text{C}_2\text{H}_4)_2\text{Ni}-\text{H}-\text{Ni}(\text{C}_2\text{H}_4)_2]^-$ (6).

which acts as a two-electron ligand toward nickel, are exactly coplanar with the nickel. The lithium cation, which has achieved its maximal coordination of four, is surrounded tetrahedrally by the two diamine ligands.

The lithium and sodium hydride in alkali metal hydridoalanes $\text{Am}[\text{AlR}_n\text{H}_{4-n}]$ and lithium diorganylphosphides LiPR_2 ($\text{R} = \text{C}_6\text{H}_{11}$, C_6H_5) also react with $(\text{C}_2\text{H}_4)_3\text{Ni}(0)$ (3) or with $(\text{COD})_2\text{Ni}(0)$ (2) and ethylene to give saltlike complexes. In contrast to the carbanions, the hydride and diorganylphosphide anion can bond two nickel atoms, giving rise to complex salts having two nickel atoms in the anion (16, 17).

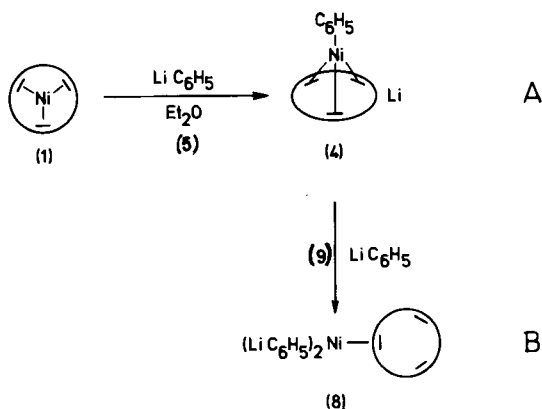


The X-ray structure analysis 7 shows that each nickel atom has a trigonal planar arrangement of ligands (14). Presumably, this is also the case for the nickel atoms in the anion of 6, for which a linear or bent 2e-3c bond $\text{Ni}-\text{H}-\text{Ni}$ can be assumed.

C. Bis(alkali metal phenyl)nickel(0) π -Ligand Complexes

Among the lithiumphenylnickel(0) π -ligand complexes of type B, the key compound is $(\text{LiC}_6\text{H}_5)_2\text{NiCDT}$ (8). It is formed at 0°C in ether from $\text{CDTNi}(0)$ (1) with 2 mol LiC_6H_5 and is isolated as crystalline $[\text{LiC}_6\text{H}_5(\text{THF})_2]_2\text{NiCDT}$ (8a) or $(\text{LiC}_6\text{H}_5\text{TMEDA})_2\text{NiCDT}$ (8b) (14) (Scheme 1).

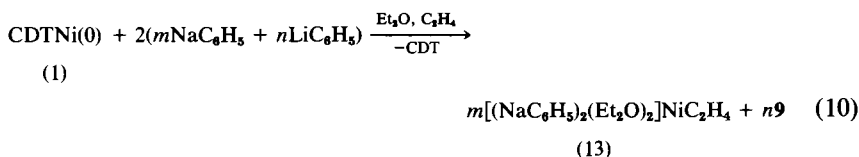
In contrast to 1 and 4, compound 8 has only one double bond of the CDT bonded to nickel, as is evident from the ^{13}C -NMR spectrum (18).



SCHEME 1

The CDT can be easily displaced by other molecules² containing multiple bonds such as alkenes, alkynes, aromatic hydrocarbons, ketones, or nitriles. New bis(phenyllithium)nickel(0) π -ligand complexes are formed, for example, with ethylene, norbornene, 3-hexyne, or phenanthrene: $[(\text{LiC}_6\text{H}_5)_2\text{Et}_2\text{O}]\text{NiC}_2\text{H}_4$ (**9**), $[(\text{LiC}_6\text{H}_5)_2\text{Et}_2\text{O}]\text{NiC}_7\text{H}_{10}$ (**10**), $\{[(\text{LiC}_6\text{H}_5)_2(\text{THF})_3]\text{Ni}\}_2\text{C}_2(\text{C}_2\text{H}_5)_2$ (**11**), and $[\text{LiC}_6\text{H}_5(\text{THF})_2]_2\text{NiC}_{14}\text{H}_{10}$ (**12**) (*14*).

The synthesis of pure bis(phenylsodium)nickel-ethylene (**13**) is achieved by reaction of a mixture of $\text{NaC}_6\text{H}_5/\text{LiC}_6\text{H}_5$ ($\text{Na}/\text{Li} = 2\text{--}4:1$) with $\text{CDTNi}(0)$ (**1**) in the molar ratio $(\text{NaC}_6\text{H}_5 + \text{LiC}_6\text{H}_5)/\text{Ni} = 2:1$ in the presence of ethylene (**19**). The phenyllithium-containing nickel-ethylene complex **9** remains dissolved while the bis(phenylsodium)nickel-ethylene (**13**) precipitates out as an orange-red powder.



$$m : n = 2\text{--}4 : 1$$

$$m + n = 1$$

The crystalline complexes $[(\text{NaC}_6\text{H}_5)_2(\text{THF})_{2.5}]\text{NiC}_2\text{H}_4$ (**13a**) and $(\text{NaC}_6\text{H}_5\text{DME})_2\text{NiC}_2\text{H}_4$ (**13b**) are obtained by exchanging the bonded ether in **13** for THF or DME.

X-Ray structures of the phenanthrene complex (**12**) and the ethylene

² For the reaction of **8** with N_2 and LiC_6H_5 see Eq. (11a) and Scheme 2 in Section II,D.

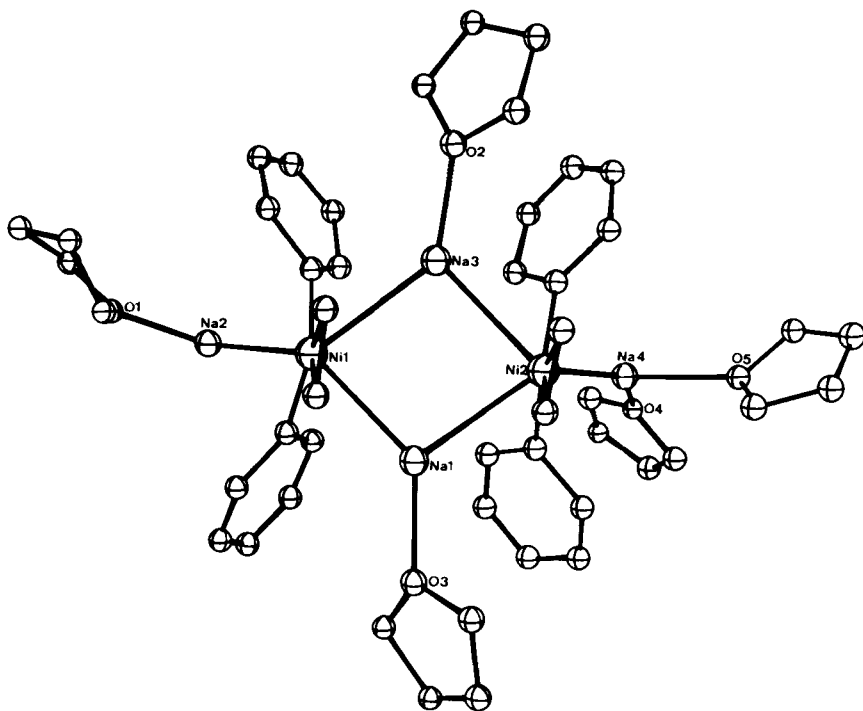


FIG. 4. Molecular structure of the complex $\{[(\text{NaC}_6\text{H}_5)_2(\text{THF})_{2.5}]\text{NiC}_2\text{H}_4\}_2$ (**13a**).

complex (**13a**) have been determined (14, 20). Figure 4 shows the molecular structure of **13a**. Compound **13a** consists of molecular units of $\{[(\text{NaC}_6\text{H}_5)_2(\text{THF})_{2.5}]\text{NiC}_2\text{H}_4\}_2$ in the crystal lattice. Four cationic sodium atoms, which are linked by carbanionic phenyl bridges, form an arched eight-membered $(\text{NaC})_4$ ring together with the four α -C atoms of the phenyl groups (Fig. 5).

Above this ring there are two mono(ethylene)nickel units, each of

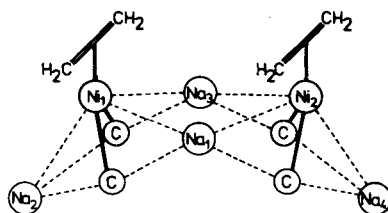


FIG. 5. Structure (schematic) of **13a**.

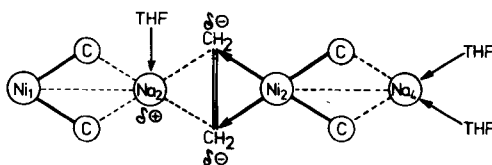
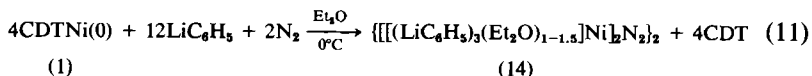


FIG. 6. Intermolecular $\text{C}_2\text{H}_4\text{Ni}(\text{C}_6\text{H}_5)_2\text{—Na—C}_2\text{H}_4\text{Ni}(\text{C}_6\text{H}_5)_2$ bridge in crystalline **13a**.

which is bonded via nickel to the α -C atoms of two carbanionic phenyl groups. These groups act as two-electron ligands toward nickel, and their α -C atoms are almost coplanar with nickel and the two ethylene C atoms. They are acting as strong donors giving appreciable charge to the π -bonded ethylene. This is reflected in both the high-field ^1H - and ^{13}C -NMR signals of the coordinated ethylene (14, 18, 19) and also in a characteristic structure element in the crystalline **13a**. Free coordination sites on all Na atoms are occupied by THF, Na1 and Na3 having one THF each while Na2 and Na4 are capable of bonding two THF molecules. However, this possibility is utilized in only one case. Na2 takes up only one THF ligand and, in addition, forms a new type of intermolecular bridge to the partially negatively charged ethylene of a neighboring $[(\text{NaC}_6\text{H}_5)_2(\text{THF})_{2.5}]\text{NiC}_2\text{H}_4$ molecule. This gives rise to a chainlike polymer structure $\{[(\text{NaC}_6\text{H}_5)_2(\text{THF})_{2.5}]\text{NiC}_2\text{H}_4\}_{2n}$ with Na2 at the rear of the Ni-ethylene bond (Na2-C: 2.75, 2.66 Å) (Fig. 6).

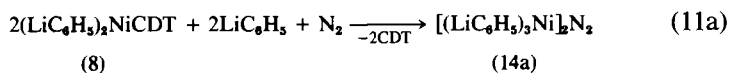
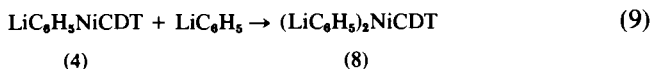
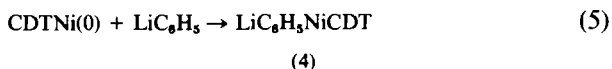
D. Dinitrogen Bonded Side-on to Nickel Atoms

The most interesting compound among the lithiumphenylnickel π -ligand complexes of type B is $\{[(\text{Li}(\text{C}_6\text{H}_5)_3(\text{Et}_2\text{O})_{1-1.5})\text{Ni}]_2\text{N}_2\}_2$ (**14**), which is formed according to Eq. (11). Both **14** and the Li and Na atoms containing Nickel- N_2 complex $\{\text{C}_6\text{H}_5[\text{NaEt}_2\text{O}]_2[(\text{C}_6\text{H}_5)_2\text{Ni}]_2\text{N}_2\text{NaLi}_6(\text{OC}_2\text{H}_5)_4\text{Et}_2\text{O}\}_2$ (**15**) are the only examples having structurally characterized side-on bonded N_2 molecules³ (22–24).



Knowing the adducts isolated from reactions of phenyllithium with $\text{CDTNi}(0)$ (**1**) (**4** and **8**) and the structure of **14**, the following mode of formation seems plausible.

³ In the X-ray structure of $\text{RhCl}(\text{N}_2)[\text{P}(\text{C}_3\text{H}_7)_3]_2$ (21) the apparent side-on coordination of dinitrogen is merely a result of statistical disorder (Cl, N_2) at an inversion center (14).



Initially, the 1:1 adduct between **1** and LiC_6H_5 is formed, and this reacts with more LiC_6H_5 to give **8**. The CDT in **8**, of which only one double bond is coordinated to nickel, is then displaced by N_2 in the presence of LiC_6H_5 . Each N_2 molecule bonds two nickel atoms, forming $[(\text{LiC}_6\text{H}_5)_3\text{Ni}]_2\text{N}_2$ units. A dimer of two such units is observed in the X-ray structure of the end product (**14**).

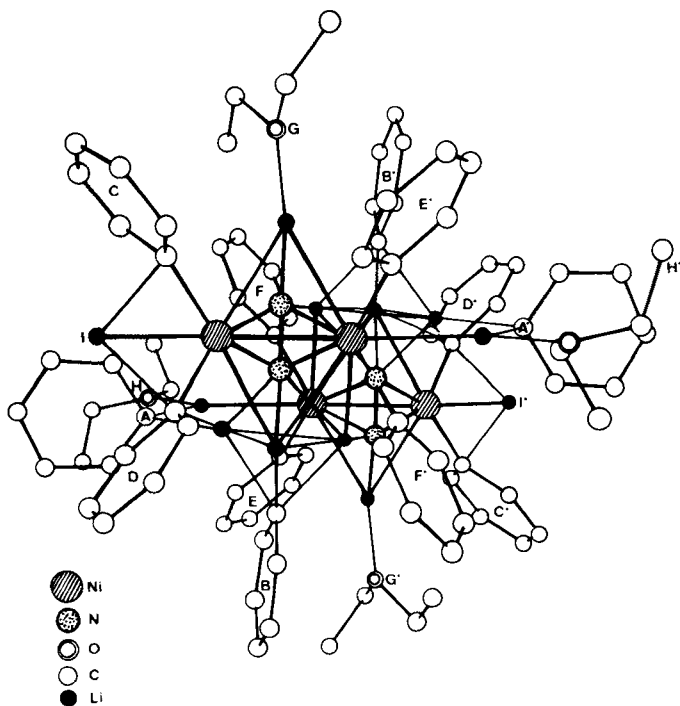


FIG. 7. Molecular structure of the centrosymmetric dimeric Li-Ni-N₂ complex $\{[(\text{LiC}_6\text{H}_5)_3(\text{Et}_2\text{O})_{1-1.5}]\text{Ni}]_2\text{N}_2\}_2$ (**14**).

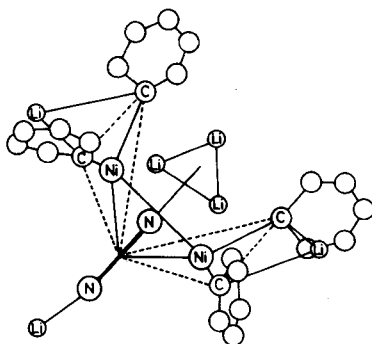


FIG. 8. Structure of the unit **14a** (schematic). The two phenyl groups bonded to the three-membered (Li—Li—Li) ring are not shown.

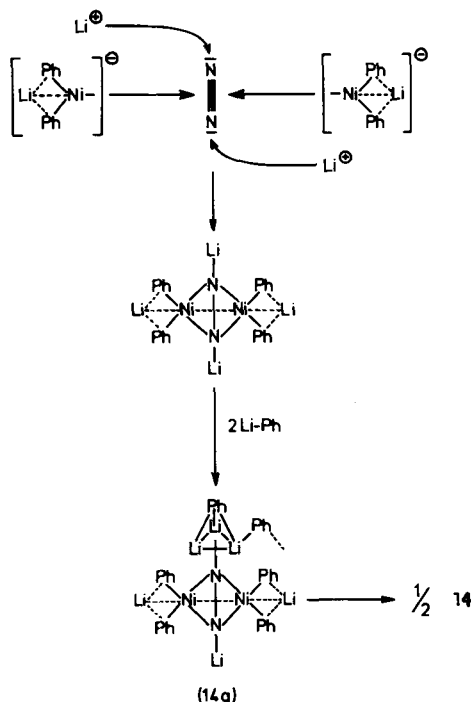
The more important structural features of one-half of the dimer, i.e., of one $[(\text{LiC}_6\text{H}_5)_3\text{Ni}]_2\text{N}_2$ unit (**14a**), are shown in Fig. 8.

The two side-on bonded Ni atoms and the two nitrogen atoms give a (Ni—Ni—N—N) tetrahedron. This structural unit, first found in **14** for a N_2 molecule, corresponds to the (Tm—Tm—C—C) tetrahedron present in binuclear transition metal—acetylene complexes (25, 26). Lithium atoms are bonded to both ends of the N_2 molecule. On one side, three Li atoms are found and on the other, only one. The N—N bond is 1.35 Å and represents a substantial lengthening compared with free N_2 (1.0976 Å) (27). This extreme elongation, and the very fact that side-on fixation to nickel is possible at all, is attributable both to the strong π -donor capacity of the two electron-rich $[\text{Ni}(\text{C}_6\text{H}_5)_2\text{Li}]$ units [$d\pi(\text{Ni}) \rightarrow \pi^*(\text{N}_2)$] and to the end-on bonded cationic Li atoms with electron-acceptor capacity [$\sigma(\text{N}_2) \rightarrow \text{Li}$ and Li_3]. The formation of **14** from $(\text{LiC}_6\text{H}_5)_2\text{NiCDT}$ (**8**), LiC_6H_5 , and N_2 in Et_2O according to Eq. (11a) can be viewed as an attack of two negatively charged $[\text{Ni}(\text{C}_6\text{H}_5)_2\text{Li}]$ units⁴ on the apolar N_2 molecule; this occurs in conjunction with the electrophilic attack⁵ of the cationic Li atoms at both ends of the N_2 molecule, giving rise to a type of an electron “push-pull” effect (Scheme 2). The inclusion of two additional LiC_6H_5 molecules, shown in Scheme 2, would give $[(\text{LiC}_6\text{H}_5)_3\text{Ni}]_2\text{N}_2$ units (**14a**) which form the dimers (**14**).

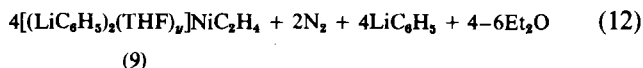
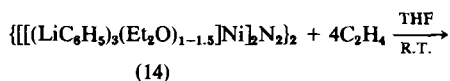
The N_2 in **14** can be displaced by carbon monoxide or ethylene. Ethylene and **14** react to give the calculated amount of N_2 and the nickel—ethylene complex (**9**), as well as free LiC_6H_5 and Et_2O (14, 22).

⁴ This unit can be derived from dimeric phenyllithium $[(\text{C}_6\text{H}_5)_2\text{LiTMEDA}]_2$ (**28**) by replacing a Li atom by Ni(0): $(\text{LiC}_6\text{H}_5)_2 + \text{Ni}(0) \rightarrow [\text{Li}(\text{C}_6\text{H}_5)_2\text{Ni}]^- + \text{Li}^+$

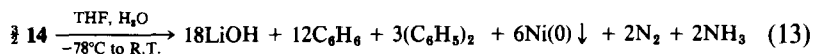
⁵ A THF solution of $\text{CDTNi}(0)$ and LiC_6H_5 does not absorb N_2 . However the Li—Ni— N_2 complex (**14**) formed in Et_2O [Eq. 11] does not liberate N_2 in THF.



SCHEME 2



On hydrolysis of **14** in THF, 30–38% of the complexed dinitrogen is reduced to ammonia, and the remainder is liberated as free N_2 . In addition to Et_2O , LiOH , and benzene, further products are biphenyl and metallic nickel. Hydrogen is not evolved.



The reduction equivalents required for conversion of N_2 to NH_3 are obtained from the carbanionic phenyl groups bonded to nickel in **14** (biphenyl formation). The Ni atoms, which are still present as $\text{Ni}(0)$, i.e., in the form of metallic nickel after hydrolysis, only function as agents for the transfer of electrons from C_6H_5^- to N_2 . In this respect, the hydrolysis of

14 differs clearly from the N_2 reduction of Chatt *et al.* (29) and Bercaw *et al.* (30) who worked with end-on bonded N_2 complexes of Mo, W, or Zr. In these cases, reduction and protonation of the N_2 ligand occur in conjunction with oxidation of the respective transition metal.

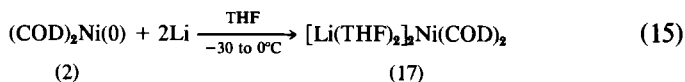
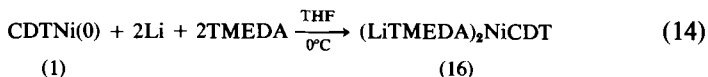
III

DILITHIUM-NICKEL-OLEFIN COMPLEXES

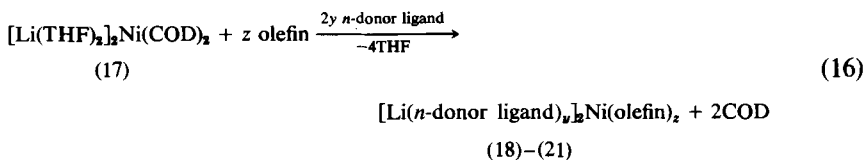
The reactions described in Section II dealt with reactions of binary nickel(0)-olefin complexes with AmR , AmH , and $AmPR_2$ and are characterized by the fact that the charge of alkali metal atoms is transferred to nickel and the respective π -ligands via C, H, or P atoms. That the charge from alkali metal atoms can also be directly transferred to nickel(0) π -ligand systems is demonstrated in the syntheses (14, 31-33), structures (14, 34), and NMR data (18, 35) of the dilithium-nickel-olefin complexes now described.

A. Syntheses and Structures of Dilithium-Nickel-Olefin Complexes

The diamagnetic dilithium-nickel-olefin complexes $(LiTMEDA)_2NiCDT$ (16) and $[Li(THF)_2]_2Ni(COD)_2$ (17) formed from $CDTNi(0)$ (1) and $(COD)_2Ni(0)$ (2) by alkali metalation, as in Eqs. (14) and (15), represent the first examples of a new class of compounds of the d-elements in which alkali metals together with olefins are bonded to transition metals (31).



Both complex-bonded COD molecules in 17 can be quantitatively displaced by monoolefins or dienes.



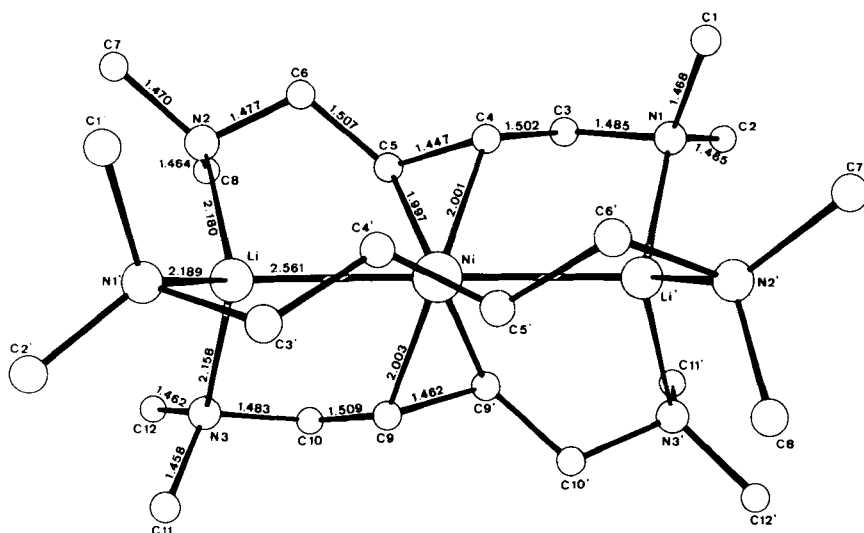


FIG. 9. Molecular structure of the complex $\text{Li}_2\text{Ni}[(\text{CH}_3)_2\text{NCH}_2\text{CHCHCH}_2\text{N}(\text{CH}_3)_2]_3$ (**18**).

Consequently, new dilithium–nickel–olefin complexes with tetra- or pentacoordinated nickel atoms are formed, e.g., the Li_2Ni complexes $\text{Li}_2\text{Ni}[(\text{CH}_3)_2\text{NCH}_2\text{CHCHCH}_2\text{N}(\text{CH}_3)_2]_3$ (**18**), $(\text{LiTMEDA})_2\text{Ni}(\text{C}_2\text{H}_4)_3$ (**19**), $(\text{LiTMEDA})_2\text{Ni}(\text{C}_7\text{H}_{10})_2$ (**20**), and $(\text{LiTHF})_2\text{Ni}(\text{C}_4\text{H}_6)_3$ (**21**), by reaction with *N,N,N',N'*-tetramethylbutene-2-diamine, ethylene, norbornene, or butadiene (14, 31–33).

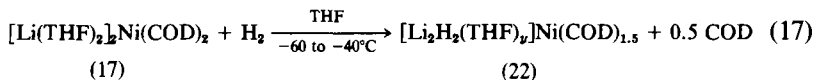
The structures of the complexes **16**, **18**, and **20** were determined by X-ray analysis (14, 34). Figure 9 shows the molecular structure of **18**.

The coordination of the nickel atom in **18** deviates only slightly from trigonal-bipyramidal geometry. The midpoints of the three double bonds are essentially coplanar with the Ni atom and define its trigonal plane. The Li atoms occupy apical positions [$\angle \text{Li}—\text{Ni}—\text{Li}'$: $178.9(1)^\circ$]. The tetra-coordinated sp^3 Li atoms which are each bonded to three amine nitrogens have a bonding metal–metal interaction (Li–Ni: 2.561 Å) and full valence shells (8-shell) as has the nickel (18-shell). The $\text{C}=\text{C}$ double bonds, considerably elongated (1.452 Å), indicate strong interactions between nickel and the olefinic double bonds.

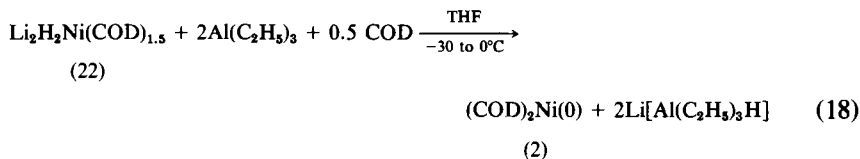
B. Nickel(0)-Induced Synthesis of Ethyllithium from Lithium, Hydrogen, and Ethylene

In general, high reaction temperatures are necessary for the synthesis of alkali metal hydrides from the elements (36), although sodium hydride

can also be formed at room temperature and normal pressure in THF if both naphthalene and titanium isopropoxide are present (37). Bis(cyclooctadiene)dilithium-nickel (**17**) reacts with molecular hydrogen (1 atm) even at -60°C . One H_2 per Li_2Ni unit is taken up with elimination of 0.5 COD/ Li_2Ni to produce the insoluble bright-yellow powder **22**.



Compound **22** contains the unchanged ligand 1,5-cyclooctadiene, as shown by reactions with cyclooctatetraene or CO in which **22** is dissolved and cyclooctadiene is liberated in high yield. Hydrogen is not evolved. This compound also dissolves in the presence of organometallic Lewis acids such as $(\text{C}_2\text{H}_5)_3\text{Al}$ if COD is added. The Li and H atoms in **22** are transferred from the complex to the $(\text{C}_2\text{H}_5)_3\text{Al}$ as lithium hydride [Eq. (18)]. Both $(\text{COD})_2\text{Ni}(0)$ (**2**) and $\text{Li}[\text{Al}(\text{C}_2\text{H}_5)_3\text{H}]$ are formed in high yields.



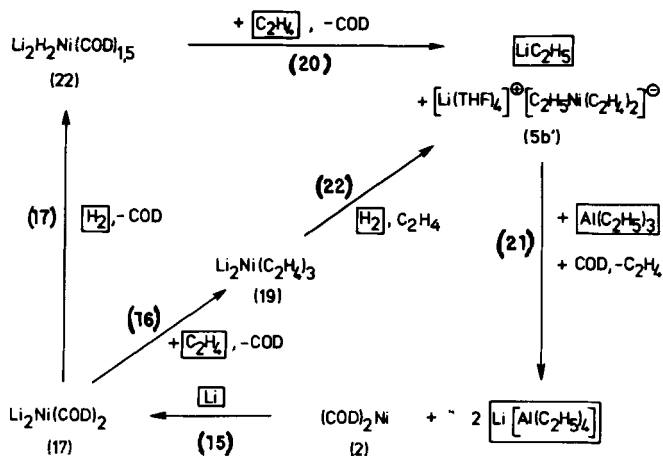
If one assumes that the lithiation of **2** gives **17** [Eq. (15)], then Eqs. (15), (17), and (18) represent a very mild nickel(0)-induced stoichiometric synthesis of $\text{Li}[\text{Al}(\text{C}_2\text{H}_5)_3\text{H}]$ from lithium, hydrogen, and $\text{Al}(\text{C}_2\text{H}_5)_3$.



An attempted nickel(0)-catalyzed synthesis of $\text{Li}[\text{Al}(\text{C}_2\text{H}_5)_3\text{H}]$, in which **2**, lithium, and $\text{Al}(\text{C}_2\text{H}_5)_3$ were allowed to react at -30°C was unsuccessful since **17** does not complex with hydrogen in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3$. However, the $(\text{COD})_2\text{Ni}(0)$ (**2**) re-formed according to Eq. (18) can be re-lithiated to start the cycle again. Thus, it is possible to synthesize $\text{Li}[\text{Al}(\text{C}_2\text{H}_5)_3\text{H}]$ in stages pseudocatalytically in a one-pot process.

Whereas pure lithium hydride prepared from lithium and H_2 does not add to $\text{C}=\text{C}$ double bonds, the "lithium hydride" bond in **22** proves to be more reactive, for example, with norbornene, propylene, or ethylene.

Compound **22** dissolves in an ethylene-saturated THF solution even at -60°C [Eq. (20)]. Cooling the clear reaction solution to -78°C leads to the crystallization of **5b'**, or of $[\text{Li}(\text{TMEDA})_2]^+[\text{C}_2\text{H}_5\text{Ni}(\text{C}_2\text{H}_4)_2]^-$ (**5b**) if TMEDA is added, while LiC_2H_5 remains in solution. Reaction of LiC_2H_5 and **5b'** with $\text{Al}(\text{C}_2\text{H}_5)_3$ and COD affords $\text{Li}[\text{Al}(\text{C}_2\text{H}_5)_4]$ and $(\text{COD})_2\text{Ni}(0)$ (**2**) according to Eq. (21); lithiation of **2** leads to regeneration of **17** [Eq.



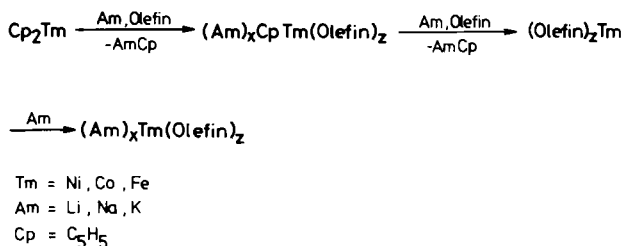
SCHEME 3

(15)]. For the preparation of $\text{LiC}_2\text{H}_5/5\text{b}'$ from 17, there is a route other than via 22 [Eqs. (17) and (20)]. This second route also involves two steps: first, displacement of the COD in 17 by ethylene, leading to the sparingly soluble 19 [Eq. (16)]; second, treatment of 19 with hydrogen and ethylene [Eq. (22)] to give a clear solution from which 5b' crystallizes on cooling to -78°C (14, 32, 38, 39). (See Scheme 3.)

IV

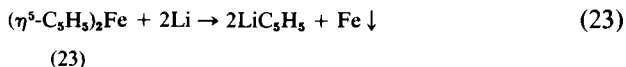
TRANSITION METAL-OLEFIN AND ALKALI METAL-TRANSITION METAL-OLEFIN COMPLEXES FROM METALLOCENES BY REDUCTIVE C_5H_5 ELIMINATION

After discovering that binary nickel(0)-olefin complexes react with lithium metal to give dilithium-nickel-olefin complexes, we were interested to find out whether alkali metal-transition metal-olefin complexes could be prepared with transition metals other than nickel. As the number of binary transition metal-olefin complexes which come into question for alkali metalation is still somewhat limited and because their preparations frequently require elaborate apparatus [co-condensation of transition metal atoms and olefins (40)], we sought a new route to this class of compounds, starting with compounds containing transition metals in higher oxidation states.



SCHEME 4

Since 1957, it has been known (41) that certain metallocenes react with alkali metals to give alkali metal cyclopentadienide and elemental transition metal as in Eq. (23).



Our investigations using $(\eta^5\text{-C}_5\text{H}_5)_2\text{Tm}$ /alkali metal systems ($\text{Tm} = \text{Ni, Co, Fe}$) showed that the precipitation of transition metals is suppressed if the metallocenes are reacted with an alkali metal in the presence of olefins (42–45).

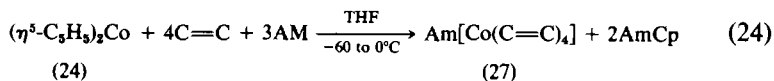
Loss of C_5H_5 rings in the form of AmC_5H_5 in THF even at low temperatures gives alkali metal-free or alkali metal-containing transition metal–olefin complexes in >65% yield. The alkali metal-containing complexes can have one or two alkali metal atoms per transition metal atom. In addition, it is possible to remove one or both C_5H_5 rings from the transition metal atom, depending on the stoichiometry, reaction conditions, and nature of the transition metal. Thus, a new route is available for preparing C_5H_5 -containing or C_5H_5 -free transition metal–olefin and alkali metal–transition metal–olefin complexes (46).

Some of the properties of $[\text{Li}(\text{THF})_2]_2\text{Ni}(\text{COD})_2$ (17), which can also be prepared from nickelocene, COD, and lithium, were discussed in Section III. Since $(\text{COD})_2\text{Ni}(0)$ (2) is an intermediate in this reaction (Scheme 4), 2 can also be prepared from nickelocene by using stoichiometric amounts of lithium (42).

A. Cobalt–Olefin and Alkali Metal–Cobalt–Olefin Complexes from Cobaltocene

$\text{Co(II)} (d^7)$ in cobaltocene (24) is reduced to $\text{Co}(-\text{I}) (d^{10})$ in the complexes $\text{Am}[\text{Co}(\text{C}=\text{C})_4]$ (27) after detachment of both C_5H_5 rings and addi-

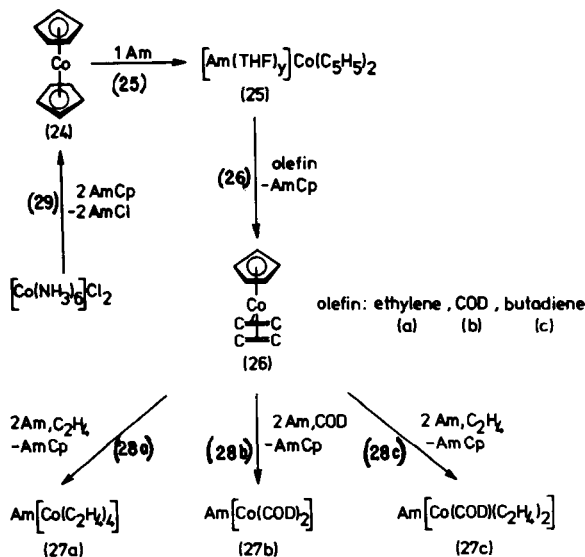
tion of an alkali metal atom to the C_5H_5 -free cobalt-olefin species. In order to convert $Co(II)$ to $Co(-I)$, which is isoelectronic with $Ni(0)$, three alkali metal atoms are required.



$C\equiv C$ = ethylene
 $(C\equiv C)_2$ = COD

Isolable alkali metal-containing and alkali metal-free intermediates are involved in the course of the formation of the new alkali metal-cobalt-olefin complexes (27) (yield 70–90%) (43, 47).

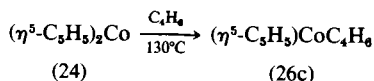
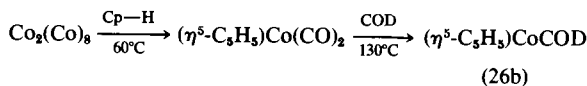
In the absence of olefins, cobaltocene (24) also reacts with excess lithium in THF at $-30^\circ C$ with addition of only one lithium atom according to Eq. (25). The $Li-Co$ complex 25 still containing both five-membered ring ligands crystallizes out of solution on cooling ($-78^\circ C$).⁶ Only under the influence of olefins does the loss of the first five-membered ring ligand in the form of $AmCp$ and the formation of $(\eta^5-C_5H_5)Co(C\equiv C)_2$ complexes (26) occur (-40 to $0^\circ C$) [Eq. (26)]. The well-known, thermally stable complexes 26b and 26c are formed when using COD and butadiene, respec-



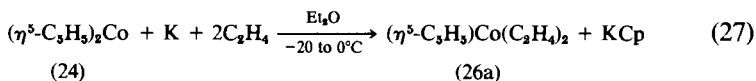
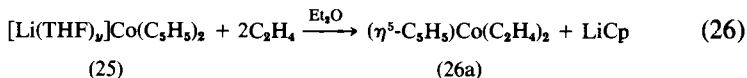
SCHEME 5

⁶ The cobaltocene anion was detected polarographically (48, 49).

tively. Thus, these compounds can also be prepared under more drastic reaction conditions, as shown here (50).



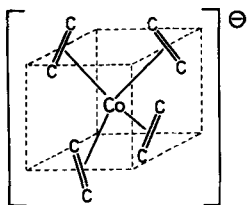
Thermally more labile $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}=\text{C})_2$ complexes such as $\eta^5\text{-cyclopentadienylbis(ethylene)cobalt}$ (**26a**) cannot be prepared by the usual methods. We prepared **26a**—the parent compound of the $(\eta^5\text{-C}_5\text{H}_5)\text{-Co-olefin}$ complexes—for the first time by reacting **25** with ethylene as in Eq. (26a) (43). A further direct route from cobaltocene (**24**) according to



Eq. (27) is also possible (47). $\eta^5\text{-Cyclopentadienylbis(ethylene)cobalt}$ (**26a**), which is stable at room temperature, can be easily prepared on a 50-g scale in 85% yield. It exhibits a wide range of interesting reactions as the ethylene ligands can be readily displaced (43, 47).

Reactions of the $(\eta^5\text{-C}_5\text{H}_5)\text{cobalt-olefin}$ complexes (**26**) prepared according to Eqs. (25) and (26) with alkali metals (Li, Na, K) in the presence of olefins lead to the elimination of the second C_5H_5 ligand from the cobalt (Scheme 5). Complexes **27a** and **27b**, or the "mixed" complex **27c** are obtained in high yields [Eq. (28)]. The syntheses of the "pure" complexes **27a** and **27b** do not, of course, require the isolation of intermediates **26a** and **26b**. As mentioned previously, synthesis is readily achieved from cobaltocene (**24**) by reaction with either stoichiometric amounts or excess alkali metal in the presence of COD or ethylene [Eq. (24)]. The alkali metal cyclopentadienides which are formed are easily separated from the cobalt complexes and can be used for the synthesis of cobaltocene (51) [Scheme 5; Eq. (29)].

In contrast to the dilithium-nickel-olefin complexes (Section III), the alkali metal-cobalt-olefin complexes $\text{Am}[\text{Co}(\text{C}=\text{C})_4]$ (**27**) have a strong tendency to dissociate into ions just as $\text{Am}[\text{Co}(\text{CO})_4]$ compounds do (52). The specific conductivities of 0.25 M THF solutions of **27** are $\kappa \approx 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ (-30°C). The values correspond to the values found for the saltlike nickel compounds **5** (Section II). That the complexes **27** can also



be prepared with the heavier alkali metals sodium and potassium is consistent with their electrolytic character.

If the C=C double bonds as in $\text{Am}[\text{Co}(\text{C}_2\text{H}_4)_4]$ (**27a**) are unrestrained, the coordination geometry of the isolated $[\text{Co}(\text{C}=\text{C})_4]$ anion would be expected to be tetrahedral ("dodecahedral" geometry). According to MO calculations on the hypothetical $(\text{C}_2\text{H}_4)_4\text{Ni}(0)$, this is the most stable ligand arrangement in olefin complexes of tetracoordinated d^{10} transition metals (53). The solution structure of the tetrakis(ethylene)cobalt anion which is in accord with the low-temperature ^{13}C -NMR spectrum of **27a** [-70°C : 55 and 37.5 ppm, R.T.: 47 ppm (^8D -THF) (*18*)] is shown schematically in Fig. 10. The crystal structure of the $\text{Li}-\text{Co}-\text{COD}$ complex (**27b**) which crystallizes from $\text{Et}_2\text{O}/\text{THF}$ with two THF molecules has been determined by X-ray methods (42).

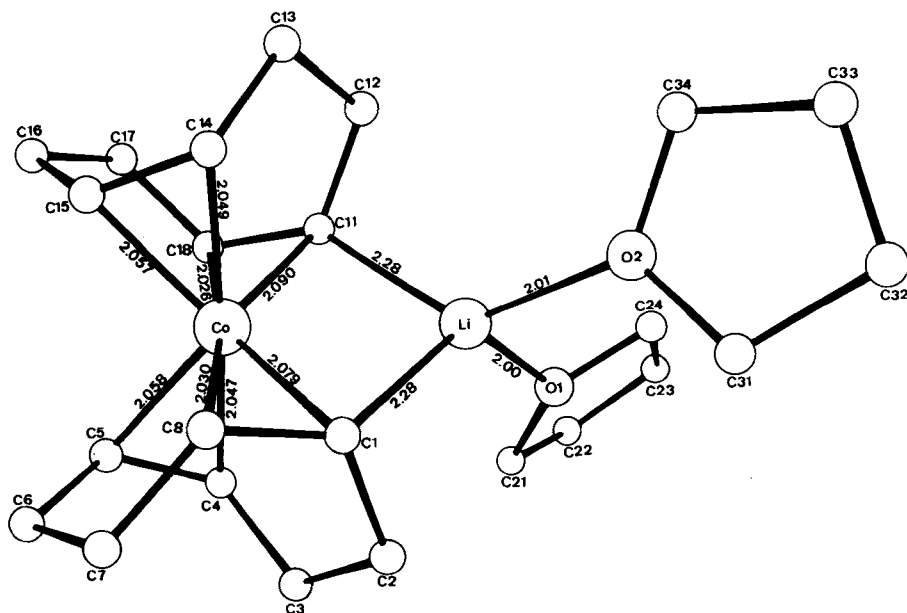
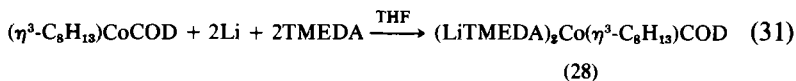
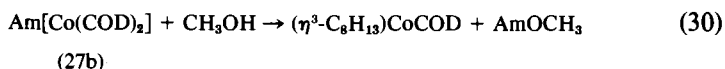


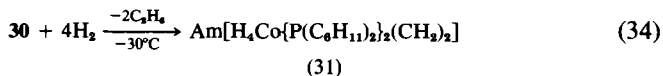
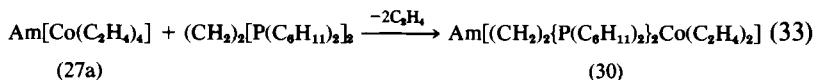
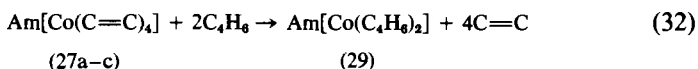
FIG. 11. Molecular structure of the complex $[\text{Li}(\text{THF})_9]\text{Co}(\text{COD})_2$ (27b).

The bond angles at the cobalt atom diverge so markedly from an ideal tetrahedron that the geometry around cobalt is better described as a trigonal bipyramid. Its equatorial positions are occupied by lithium and by two double bonds of the two olefinic ligands [C1–C8: 1.413(7) Å, C11–C18: 1.419(7) Å]. As a result of bridging between equatorial and axial positions of the cobalt [C4–C5: 1.391(8) Å, C14–C15: 1.401(8) Å], the COD ligands assume a highly distorted boat conformation. Short Li–C distances [Li–C1, Li–C11] indicate a strong ion-pair interaction (14, 54) between the tetrahedrally coordinated Li atom and C atoms of the double bonds in equatorial positions. The Li–Co distance [2.654(8) Å] is approximately equal to the sum of the respective covalent radii.

The compounds $\text{Am}[\text{Co}(\text{COD})_2]$ (**27b**) react with methanol according to Eq. (30) to give the known η^3 -cyclooctenyl(η^4 -1,5-cyclooctadiene)-cobalt (55–57). This complex reacts with lithium metal in a similar way to nickel(0)-olefin complexes. Two lithium atoms are added to give **28** (46).

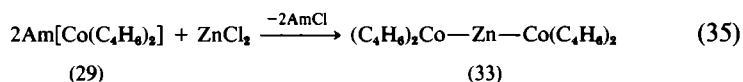


The two coordinated COD molecules in $\text{Am}[\text{Co}(\text{COD})_2]$ (**27b**) and the four bonded ethylenes in $\text{Am}[\text{Co}(\text{C}_2\text{H}_4)_4]$ (**27a**) are readily displaced by CO or butadiene at low temperatures as in Eq. (32) (42, 43). The diphosphane $(\text{CH}_2)_2[\text{P}(\text{C}_6\text{H}_{11})_2]_2$ displaces only two ethylene molecules from **27a** at 0°C giving **30**. These latter compounds ($\text{Am} = \text{Li}, \text{K}$) react with hydrogen to yield novel alkali metal-containing hydridocobalt-phosphane complexes (**31**) which have 2H_2 per AmCo (47).



As in the anion of **29**, the cobalt-bonded butadiene ligands in the new complexes $\text{R}_3\text{Sn}-\text{Co}(\text{C}_4\text{H}_6)_2$ (**32**) ($\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) and $\text{Zn}[\text{Co}(\text{C}_4\text{H}_6)_2]_2$ (**33**) are not coupled. Compounds **32** and **33** which are formed by reaction

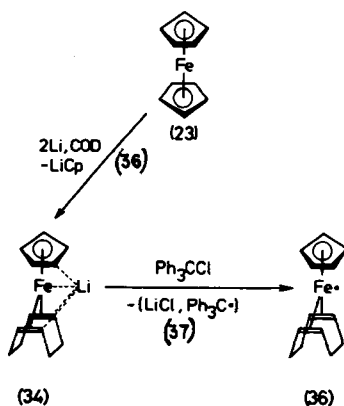
of, respectively, R_3SnCl and $ZnCl_2$ with **29** are stable at room temperature.



B. Iron–Olefin and Alkali Metal–Iron–Olefin Complexes from Ferrocene

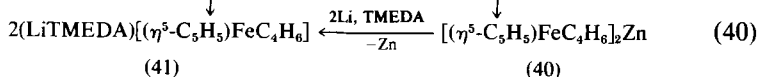
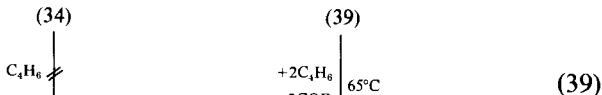
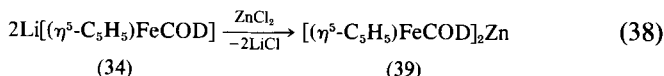
As for cobaltocene, it is also possible systematically to substitute one or both C_5H_5 ligands in ferrocene (**23**) by olefins and alkali metal (**44–46**, **58**). Reaction of ferrocene (**23**) at low temperature (-60 to $-40^\circ C$) in DME or THF with lithium and COD or ethylene leads, via exchange of only one C_5H_5 ligand, to the formation of the iron complexes $(LiDME)(\eta^5-C_5H_5)FeCOD$ (**34a**) or, after addition of TMEDA, to crystalline $(LiTMEDA)(\eta^5-C_5H_5)FeCOD$ (**34b**) or $(LiTMEDA)(\eta^5-C_5H_5)Fe(C_2H_4)_2$ (**35**). Treatment of **34a** with trityl chloride affords η^5 -cyclopentadienyl- $(\eta^4-1,5\text{-cyclooctadiene})iron$ (**36**), which, in contrast to the dimeric $[(C_5H_5)Fe(CO)_2]_2$ (**37**) (**59**, **60**), is obtained as the monomer with an unpaired electron (Scheme 6).

The olefins coordinated in **34–36** can be displaced by CO (1 atm) even at low temperatures. Compound **36** and CO react to give **37**, whereas **34** and **35** yield $Li[(\eta^5-C_5H_5)Fe(CO)_2]$, which can be isolated as crystalline $(LiTMEDA)(\eta^5-C_5H_5)Fe(CO)_2$ (**38**). The corresponding sodium compound is known in solution (**59**, **61**).



SCHEME 6

Complexes **34** and **35** (44, 58), and in particular the Fe(I) compound **36** (62), are suitable starting materials for the syntheses of a large number of organoiron compounds. For example, complexes **34** and **35** react with metal halides such as ZnCl_2 or CdCl_2 to give new trinuclear complexes having olefin ligands bound to iron atoms; for example,

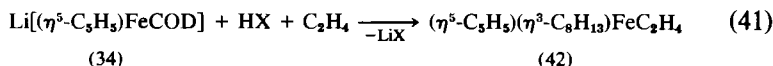


(41)

(40)

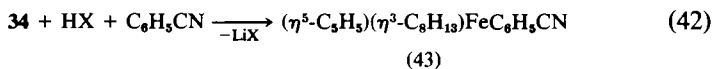
Replacement of cyclooctadiene in the zinc derivative **39** by butadiene leads to the trinuclear complex **40**, which can be converted by reaction with lithium metal into **41** and metallic zinc. Under mild reaction conditions, **41** cannot be obtained directly from **34** and butadiene.

The lithium-iron complex **34** reacts with HX compounds [$(\text{CH}_3)_3\text{COH}$, CH_3OH , CH_3COOH] in the presence of either ethylene or benzonitrile with addition of the Fe-H bond to a double bond of the eight-membered ring and isomerization of the $\text{Fe-C}_8\text{H}_{13}$ group to yield the new Fe(II) complexes $\eta^5\text{-cyclopentadienyl}(\eta^3\text{-cyclooctadienyl})\text{iron-ethylene}$ (**42**) and $\eta^5\text{-cyclopentadienyl}(\eta^3\text{-cyclooctadienyl})\text{iron-benzonitrile}$ (**43**), respectively. Both complexes react with CO , eliminating C_2H_4 or $\text{C}_6\text{H}_5\text{CN}$ and giving complex **44** which is stable at room temperature (58).

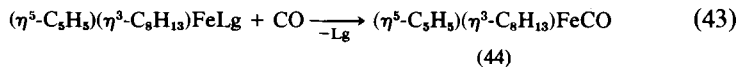


(34)

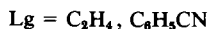
(42)



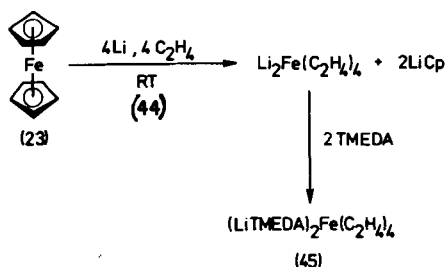
(43)



(44)



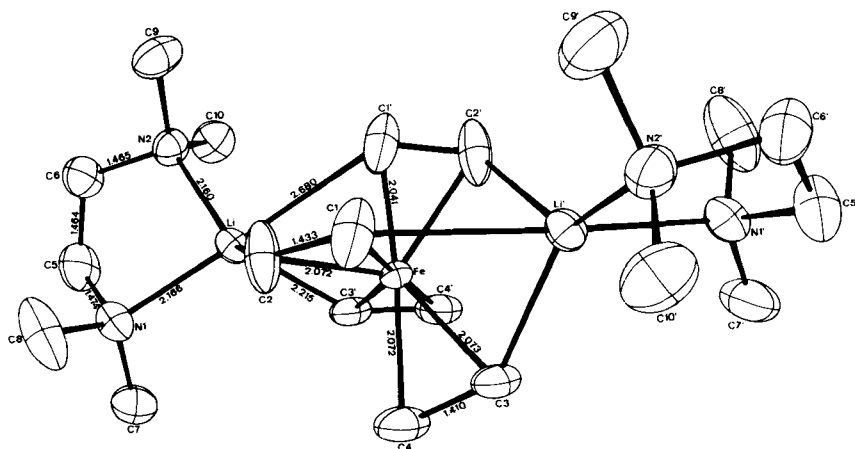
If one reacts ferrocene (**23**) with lithium metal and ethylene in THF at room temperature, both C_5H_5 rings are eliminated and tetrakis(ethylene)dilithium iron, which is isolated as crystalline $(\text{LiTMEDA})_2\text{Fe}(\text{C}_2\text{H}_4)_4$ (**45**), is formed.

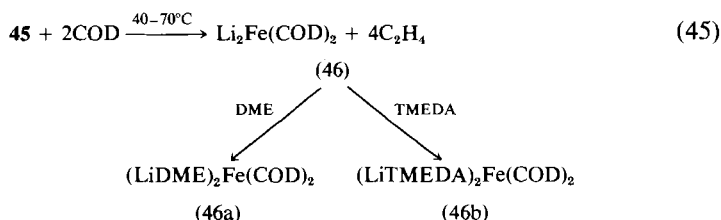


SCHEME 7

The X-ray structure analysis of **45** (14, 45) shows that the central Fe atom is in a distorted octahedral environment with four equatorial C_2H_4 ligands and two Li atoms occupying the apical positions. The iron–olefin moiety has approximately the geometry expected for d^{10} systems with ethylene ligands (53). A twofold crystallographic axis passes through the iron atom and bisects the C1–C1' vector. Short Li–C distances [Li–C2 2.174; Li–C3' 2.215 Å], as in $[\text{Li}(\text{THF})_2]\text{Co}(\text{COD})_2$ (**27b**) (Fig. 11), indicate strong ion-pair interactions between the tetrahedrally coordinated Li atom and the olefin C atoms.

At -78°C , **45** reacts with carbon monoxide (1 atm) with uptake of four equivalents of CO and liberation of four equivalents of ethylene. Reaction of **45** with COD at $40\text{--}70^\circ\text{C}$ affords $\text{Li}_2\text{Fe}(\text{COD})_2$ (**46**) isolated as the crystalline **46a** and **46b**.





The preparation of **46** completes the series of isoelectronic transition metal–cyclooctadiene complexes of the 3d elements of subgroup 8—namely (COD)₂Ni(0) (**2**), Am[Co(COD)₂] (**27b**) and Li₂Fe(COD)₂ (**46**).

The method involving reductive C_5H_5 removal using alkali metals can also be applied to other η^5 -cyclopentadienyl transition metal compounds. In addition, other ligands such as phosphanes, carbon monoxide or dinitrogen can be used instead of olefins.

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Organic Compounds of Divalent Tin and Lead

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I

INTRODUCTION

While the inorganic chemistry of divalent tin and lead is well established, there are few well-characterized divalent organotin and organo-lead compounds. The " R_2Sn " formulation seen in the older literature has proved to be an empirical formula, the formally divalent stannylene actually being an oligomeric linear or cyclic organostannane. Neumann has commented on this point several times (1-3).

This review focuses on the preparation, structure, and chemical and

physical properties of isolable compounds of divalent tin and lead containing direct metal-to-carbon bonds. Isoelectronic stannylamines as well as structurally related germynes are dealt with where appropriate. Divalent tin alkoxides, carboxylates, acetylacetonates, etc. are not dealt with here since these compounds have been thoroughly covered in reviews of inorganic divalent tin and lead (4-6). Divalent alkyl and aryl tin compounds existing only as reactive intermediates are not covered here. The reader is referred to the recent review (3) and articles (7-11) in this area.

Divalent organotin and organolead compounds can be divided into two classes, viz, those in which the organic groups are σ -bonded and those in which the organic groups are π -bonded to the metal. We will deal with these two classes separately beginning with the π -bonded species. A third section will cover transition metal stannylene and plumbylene complexes from both classes.

II

π -BONDED COMPOUNDS

A. Structure

Stannocene, bis- η^5 -cyclopentadienyltin(II), and plumbocene, bis- η^5 -cyclopentadienyllead(II), were first reported by Fischer and Gruber in 1956 (12). They observed the compounds to be monomeric in benzene and to have nonzero dipole moments and proposed the σ -bonded structure shown in Fig. 1A. Wilkenson and co-workers reported the similarity between the IR spectrum of stannocene, plumbocene, and ferrocene and suggested the presently accepted angular sandwich structure for stannocene and plumbocene shown in Fig. 1B (13).

The local symmetry in pentahapto cyclopentadienyl complexes is D_{5h} while in monohapto species it is C_s . Due to this large change in symmetry, vibrational spectroscopy has been a useful tool in distinguishing between the σ - and π -modes of bonding. Maslowsky has summarized this in some

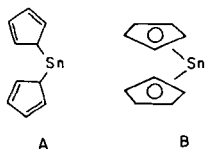


FIG. 1. (A) σ -Bonded and (B) π -bonded structures for stannocene and plumbocene.

detail (14). A complete assignment of the vibrational spectrum of stannocene has been reported (15).

The gas-phase structures of stannocene and plumbocene have been determined by electron diffraction (16). The radial distribution curves were fitted using angular sandwich model structures. The derived $\text{Cp}-\text{M}-\text{Cp}$ angles were 135° for plumbocene and 125° for stannocene, but it is not clear that the difference is real.

The solid-state structure for stannocene has not been determined; the crystal structure for the orthorhombic crystalline form of plumbocene is shown in Fig. 2 (17). Plumbocene is associated in the solid state, with each lead atom coordinated to three cyclopentadienyl rings, one of them terminal and two of them bridging to other lead atoms.

In keeping with the greater metallic character of lead, divalent organo-lead compounds appear to be more associated in the solid state than corresponding divalent organotin compounds. On the basis of its high melting point, $330-360^\circ\text{C}$, CpPbCl is assumed to have a polymeric structure (18). The corresponding tin compound CpSnCl has a melting point of $130-133^\circ\text{C}$ (19), and the crystal structure, shown in Fig. 3, is clearly monomeric (20). Each tin has a bonded chlorine $\text{Sn}-\text{Cl}$ distance of 2.68 \AA , and is associated to two other chlorines at 3.24 and 3.26 \AA . Interestingly, the

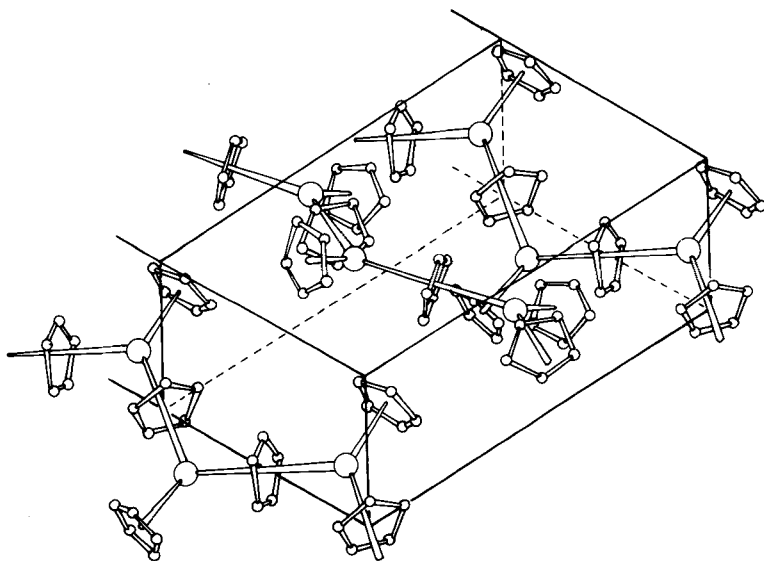


FIG. 2. A perspective view of the chains in PbCp_2 (17). Reprinted with permission from *Acta Crystallogr.* **21**, 823 (1966). Copyright by the International Union of Crystallography.

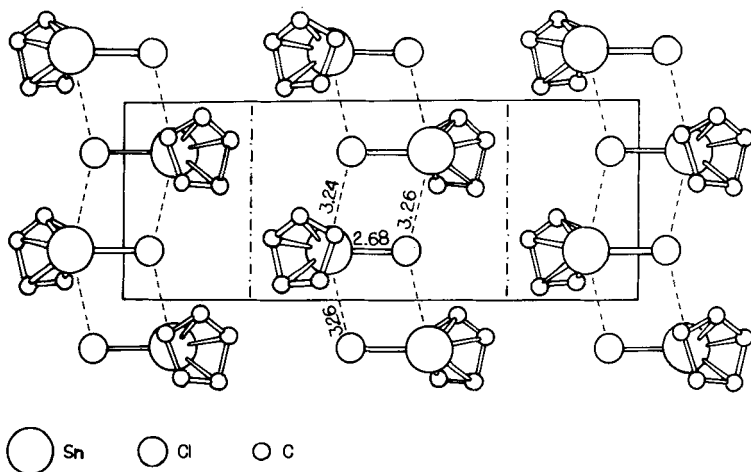


FIG. 3. Crystal structure of C_5H_5SnCl (20). Reprinted with permission from *J. Organomet. Chem.* **99**, 71 (1975). Copyright by Elsevier Sequoia S. A.

cyclopentadienyl ring is asymmetrically bonded to tin, with Sn—C bonds ranging from 2.45 to 2.74 Å with an average Sn—C bond length of 2.68 Å.

Bis(pentamethylcyclopentadienyl)tin(II) has been synthesized (21) and its crystal structure determined (22). It is monomeric in the solid state, with asymmetrically bound cyclopentadienyl rings, the Sn—C distance ranging from 2.585 to 2.766 Å, averaging 2.69 Å. The Cp—Sn—Cp angles in the two different crystal environments of this compound are 143.6° and 144.6°, considerably wider than the 125° angle found for stannocene in the gas phase (16).

The crystal structure for pentamethylcyclopentadienyltin(II) tetrafluoroborate has been determined (23) and is shown in Fig. 4. The Sn—C bonds are all equal and quite short at 2.462 Å. Apparently, the Sn—Cp bonding is stronger in the +1 ion than in the neutral $SnCp_2$ species. Each tin atom is associated to two fluorine atoms of the BF_4^- counterion at distances of 2.97 and 2.99 Å.

Several η^6 -arene complexes of divalent tin and lead have been synthesized by Amma and co-workers (24–28). The crystal structure for η^6 - $C_6H_6SnCl(AlCl_4)$ is shown in Fig. 5 (28). The arene is bonded at an average Sn—C distance of 3.2 Å, considerably longer than in the cyclopentadienyl derivatives. The structure consists of planar $Sn_2Cl_2^{2+}$ units with each tin chelated by two chlorine atoms of an $AlCl_4^-$ and additionally bound to one chlorine of another $AlCl_4^-$, which generates a chain structure. The coordination of the tin is completed by the asymmetrically bound arene with Sn—C distances from 3.05 to 3.39 Å. The related com-

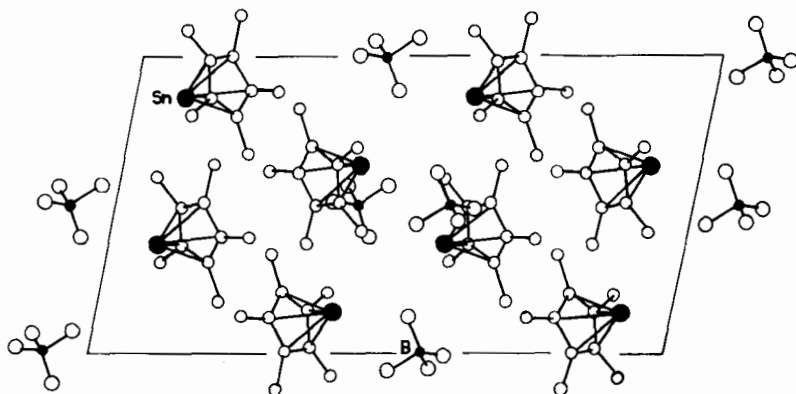


FIG. 4. Crystal structure of $(\text{Me}_3\text{C}_3)\text{SnBF}_4$ (23). Reprinted with permission from *Angew. Chem., Int. Ed. Engl.* **18**, 59 (1979). Copyright by Verlag Chemie.

plex $\eta^6\text{-}p\text{-(CH}_3)_2\text{C}_6\text{H}_4\text{SnCl(AlCl}_4\text{)}$ also has the arene asymmetrically bound. This asymmetry is attributed to crystal packing forces, and not to any intrinsic electronic effect between the tin and aromatic ring (28). The arene complexes $\eta^6\text{-C}_6\text{H}_6\text{M(AlCl}_4)_2\cdot\text{C}_6\text{H}_6$ [$\text{M} = \text{Sn}$ (24), $\text{M} = \text{Pb}$ (26)] contain symmetrically bound benzene rings.

B. Synthesis

Stannocene and plumbocene are synthesized by the salt elimination method shown in Eq. (1) (12).

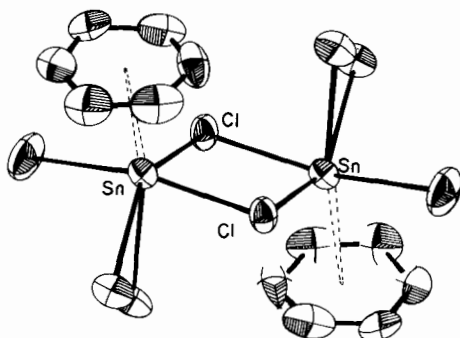
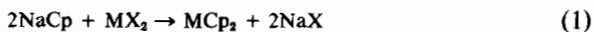
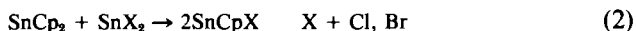


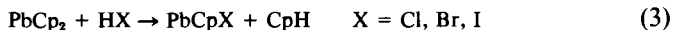
FIG. 5. Crystal structure of $\eta^6\text{-C}_6\text{H}_6\text{SnCl(AlCl}_4\text{)}$ (28). Reprinted with permission from *Inorg. Chem.* **18**, 751 (1979). Copyright by the American Chemical Society.

This same method has been used to synthesize germanocene (29), the bis-methylcyclopentadienyl divalent Ge (30), Sn (13), and Pb (13) compounds, and bispentamethylcyclopentadienyltin(II) (22).

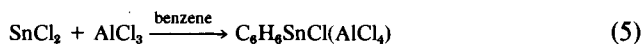
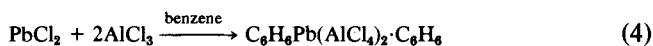
Cyclopentadienyltin(II) chloride and bromide can be made by the exchange reaction shown in Eq. (2) (19). This is apparently an equilibrium system, and the product is determined by the relative solubility of the reagents present. It is not possible to synthesize the iodide this way because it is too soluble in THF (31).



Cyclopentadienyllead(II) halides are synthesized by reaction of plum-bocene with the hydrogen halide in benzene as shown in Eq. (3). The products precipitate out and high yields are obtained (18).



The arene complexes are made by direct reaction of the arene with the $\text{MCl}_2/\text{AlCl}_3$ adducts as shown in Eqs. (4) and (5) (26, 28).



Other derivatives containing π -bound ligands are synthesized as discussed in the following section.

C. Reactions

The angular sandwich structure for stannocene is best explained by proposing sp^2 hybridization for the tin atom. As a result, tin has a lone pair of electrons and an empty p_z orbital. Stannocene commonly behaves as a Lewis base, donating its electron pair. However, stannocene does not form stable complexes with Lewis bases, which suggests that the empty p_z orbital is used to accept electron density from the filled cyclopentadienyl e orbitals.

A number of reactions have been reported in which the tin in stannocene is converted from tin(II) to tin(IV). When the cyclopentadienyl group is retained in such a reaction it becomes a monohapto group. Perhaps the best example of this type of reaction is the polymerization of stannocene, shown in Eq. (6) (32).



In this regard the π -bonded stannocene is similar to most of the σ -bonded stannylenes which polymerize as soon as they are formed. Stannocene

does not spontaneously polymerize in the solid state at room temperature, but its polymerization is catalyzed by bases such as DMF. The tin contained in polystannocene has been shown by its Mössbauer spectrum (Table II) to be tetravalent (31).

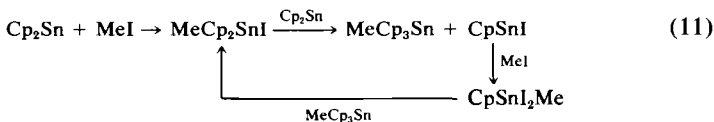
In keeping with the increased stability of the divalent state on descending group IV, germanocene undergoes polymerization in three hours (29) and plumbocene shows no tendency to polymerize.

There are many instances in which the pentamethylcyclopentadienyl metal compounds are more stable than the cyclopentadienyl compound (33, 34), and the stannocene system is no exception. Thus, decamethylstannocene is air stable for several hours at room temperature whereas stannocene (and polystannocene) are oxidized rapidly on exposure to air. Decamethylstannocene can be stored at room temperature under nitrogen for prolonged periods (21).

Polymerization of stannocene can be considered an oxidative addition reaction. Other examples of oxidative addition are shown in Eqs. (7–10) (35, 36).



These reactions may not be as straightforward as they appear. The reaction shown in Eq. (7) is considered to proceed by a radical mechanism since it does not occur in the dark (6). As is discussed in Section III,C, Lappert and co-workers have shown that the oxidative addition reactions of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ occur by a free radical process. A mechanism suggested for Eq. (7) on the basis of the initial appearance of CpSnI and some NMR evidence is shown in Eq. (11) (36).



Similar reactions with plumbocene do not lead to $\text{Pb}(\text{IV})$ compounds, but to $\text{Pb}(\text{II})$ compounds as shown in Eqs. (12) and (13) (18).

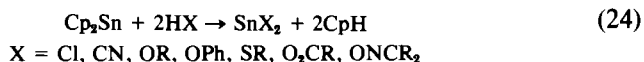


Equation (13) is thought to proceed through the intermediate $\text{Cp}_2\text{Pb}(\text{CH}_3)\text{I}$, analogous to Eq. (11). Precedent for this proposed reduc-

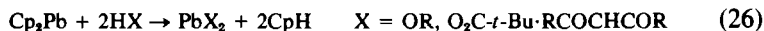
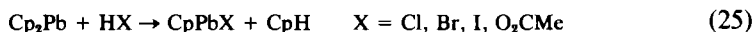
which appears to be associated in the solid state. The proposed structure for $\text{Cp}_2\text{Pb}:\text{BF}_3$ is shown in Fig. 6 (41).

Tetracyanoethylene (tcne) and 7,7,8,8-tetracyanoquinodimethane (tcnq) both form adducts with stannocene and plumbocene that are of uncertain structure. The stannocene derivatives $\text{SnCp}_2:(\text{tcne})_n$ ($n = 1$ or 2) and $\text{SnCp}_2:(\text{tcnq})$ are proposed to be cyclopentadienyl π -charge transfer complexes (42). The plumbocene derivatives $\text{PbCp}_2:(\text{tcne})_n$ ($n = 0.5$ or 1) and $\text{PbCp}_2:(\text{tcnq})$ apparently involve charge transfer and are proposed to be polymeric (41).

Protolytic cleavage of the $\text{Sn}-\text{Cp}$ bond of stannocene is a reaction of great synthetic utility in the synthesis of a variety of divalent tin compounds. In some cases the partially substituted product CpSnX can be isolated, but in most reports SnX_2 is synthesized according to Eq. (24) (43–49).



The methycyclopentadienyl analog of stannocene undergoes similar reactions. Plumbocene (18) undergoes the protolytic cleavage reactions shown in Eqs. (25) and (26).



The reaction between triphenylsilanol and stannocene (31) gives the equilibrium mixture shown in Eq. (27).



Protolysis has also been observed in the reaction between stannocene and the transition metal hydrides shown in Eqs. (28) (50), (29) (51), and (30) (44, 52).

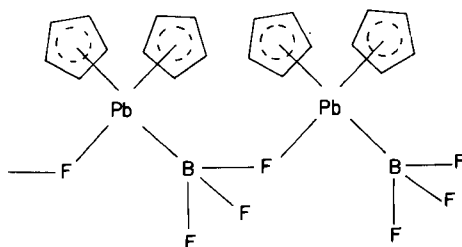
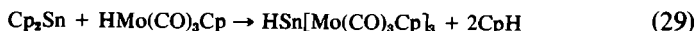
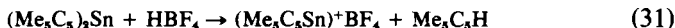


FIG. 6. Proposed structure of $\text{Cp}_2\text{Pb}:\text{BF}_3$ (41). Reprinted with permission from *J. Chem. Soc., Dalton Trans.* p. 228 (1979). Copyright by The Chemical Society.

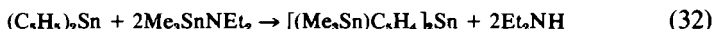


Bis(pentamethylcyclopentadienyl)tin(II) undergoes protolytic cleavage of one pentamethylcyclopentadienyl group to yield the salt $\text{Me}_5\text{C}_5\text{-Sn}^+\text{BF}_4^-$ as shown in Eq. (31) (23).



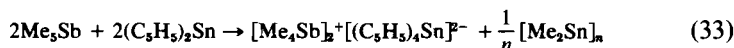
The mass spectrum of stannocene (and plumbocene) is dominated by the CpSn^+ (or CpPb^+) ion (see Section II,D), but Eq. (31) represents the first isolation of a stable form of this species.

The first synthesis of an organometallic compound containing both divalent and tetravalent tin has been performed according to Eq. (32).



The product, a yellowish-green oil, has been characterized by NMR and Mössbauer spectroscopy (53).

Stannocene reacts with pentamethylantimony according to Eq. (33).



This represents the first synthesis of an anionic organotin(II) derivative; it has been characterized by its elemental analysis, NMR, and Mössbauer spectroscopy but the compound's structure is not known (54).

D. Spectroscopic Properties

Due to their volatility, a number of stannocene and plumbocene derivatives have been studied by mass spectroscopy. The dominant feature in the mass spectrum of Cp_2Sn , $\text{Cp}_2\text{Sn}:\text{BF}_3$ (39), CpSnCl (31), $(\text{Me}_5\text{C}_5)_2\text{Sn}$ (21), Cp_2Pb , CpPbCl , CpPbBr , and CpPbI (18) is the $\text{R}_5\text{C}_5\text{M}^+$ ion ($\text{R} = \text{Me}$ or H). Apparently, redistribution occurs when CpMX is volatilized since

¹ The product of Eq. (29) has been characterized by C, H, Sn, and Mo elemental analysis, solution molecular weight, and NMR data. Furthermore it has been shown to react with halogenated hydrocarbons to produce the corresponding tin halide [as does the product of Eq. (28)]. The product of Eq. (30) was so formulated on the basis of C and H analysis, solution molecular weight, and Mössbauer data. However, the compound was obtained by recrystallization from methylene chloride. The authors think it is likely that the product of Eq. (30) is $\text{HSn[W(CO)}_5\text{Cp}]_2$ which is converted in work-up to $\text{ClSn[W(CO)}_5\text{Cp}]_2$. The C,H analysis and Mössbauer data are consistent with this as is the molecular weight (1007) which is closer to $\text{ClSn[W(CO)}_5\text{Cp}]_2$ (1156) than the proposed $\text{Sn[W(CO)}_5\text{Cp}]_2$ (784).

the mass spectrum contains peaks due to Cp_2M and SnX_2 as well. Sublimation of CpSnCl at 130°C at 10^{-4} mm results in a product with more cyclopentadienyl groups than chlorine atoms (31).

$^{117,119}\text{Sn}-\text{H}$ coupling, $J_{\text{Sn}-\text{H}} = 15.9$ Hz, is shown by the room-temperature NMR spectrum of stannocene. At 125°C in toluene this coupling disappears, suggesting the onset of dissociative processes. No $\text{Sn}-\text{H}$ coupling is seen in CpSnCl even at -80°C , indicating intermolecular exchange (32).

The bismethylcyclopentadienyl derivatives of divalent germanium, tin, and lead have been studied by ^1H , ^{13}C -, and ^{119}Sn -NMR spectroscopy (30). Since the ^1H and ^{13}C spectra of all these compounds are quite similar, it was concluded that all three compounds in solution have the angular sandwich structure. At ambient temperature the ^{13}C -NMR spectrum of the tin compound does not show $\text{Sn}-\text{C}$ coupling; however, upon lowering the temperature to -55°C coupling was observed. This was interpreted in terms of intermolecular exchange at ambient temperature. The ^{13}C -chemical shifts, shown in Table I are indicative of an increasing ionic character to the $\text{M}-\text{Cp}$ bond upon descending group IV.

The ^{119}Sn -NMR spectrum at -40°C shows a nonet structure, indicating equivalent coupling of the eight ring protons of the two bound methylcyclopentadienyl rings. The chemical shift of the tin nucleus, 2171.1 ppm upfield from tetramethyltin, contrasts with the value of -27.2 ppm determined for the tin(IV) cyclopentadienyl derivative SnCp_4 . This difference is attributed to the increase in shielding expected for the divalent derivative.

As mentioned earlier, papers have appeared on the vibrational spec-

TABLE I
 ^{13}C CHEMICAL SHIFTS^a FOR METHYLCYCLOPENTADIENYL DERIVATIVES
OF DIVALENT Ge, Sn, AND Pb^b

Compound	$\delta(\text{C}_1)^c$	$\delta(\text{C}_{2,5})^c$	$\delta(\text{C}_{3,4})^c$	$\delta(\text{C}_{\text{Me}})$	Solvent
$\text{Ge}(\text{C}_5\text{H}_4\text{CH}_3)_2$	126.2	113.0	110.5	14.1	CDCl_3
$\text{Sn}(\text{C}_5\text{H}_4\text{CH}_3)_2$	123.6	110.8	108.5	14.0	CDCl_3
$\text{Pb}(\text{C}_5\text{H}_4\text{CH}_3)_2$	114.3	104.7	103.7	14.6	C_6H_6
$\text{Li}(\text{C}_5\text{H}_4\text{CH}_3)$	113.1	103.1	101.7	14.4	Monoglyme
$\text{K}(\text{C}_5\text{H}_4\text{CH}_3)$	113.4	104.0	102.9	14.7	Monoglyme
$\text{Tl}(\text{C}_5\text{H}_4\text{CH}_2)$	<i>d</i>	107.5	105.0	<i>d</i>	Monoglyme

^a At 300°K , downfield from $\text{Me}_4\text{Si} = 0$ ppm.

^b From Bonny *et al.* (30).

^c Carbon atoms of the Cp ring numbered sequentially around ring, with methyl-substituted carbon = C_1 .

^d Not observed due to low solubility of Tl(I) derivative.

troscopy of stannocene and related compounds (15, 55). Infrared spectroscopy is apparently of greatest value in distinguishing between pentahapto and monohapto bonding of the cyclopentadienyl group. On the basis of IR evidence, the cyclopentadienyl rings in $\text{Cp}_2\text{Sn}:\text{BF}_3$ have been proposed as being pentahapto (39).

Mössbauer spectroscopy has proved to be a very valuable tool in tin chemistry. The isomer shift (IS) is a measure of the 5s electron density at the tin nucleus while the quadrupole splitting (QS) is a measure of the electric field gradient (due to the asymmetry of the electron cloud) at the tin nucleus. On going from the plus two to the plus four oxidation state tin loses 5s electron density. Since the tin nucleus expands on absorption of the 23.9 keV photon during the Mössbauer experiment, the greater the s electron density at the nucleus the more positive the isomer shift will be (56, 57). Therefore, tin(II) compounds have higher isomer shift values than do tin(IV) compounds. The isomer shift of β tin (2.56 mm/sec relative to BaSnO_3) is commonly used as the dividing point between divalent and tetravalent tin (58–60).

The data listed in Table II (15, 27, 31, 32, 39, 40, 42, 53, 54, 61) indicate

TABLE II
MÖSSBAUER DATA FOR π -BONDED STANNYLENES

Compound	Isomer shift	Quadrupole splitting	Reference
SnCl_2	4.13	0	61
SnCp_2	3.73	0.65	32
$(\text{SnCp}_2)_n$	0.72	0	32
$\text{Sn}(\text{MeC}_5\text{H}_4)_2$	3.83	0.78	15
CpSnCl	3.71	1.04	40
CpSnBr	3.40	0.99	31
CpSnI	3.90	0	31
$(\text{MeC}_5\text{H}_4)_2\text{SnAlCl}_3$	3.71	0	40
$\text{Cp}_2\text{SnAlCl}_3$	3.71	0	40
$\text{Cp}_2\text{SnAlBr}_3$	3.83	0	40
$\text{Cp}_2\text{SnBBBr}_3$	3.77	0	40
Cp_2SnBF_3	3.79	0.90	39
CpSnAlCl_4	3.73	0	40
$\text{CpSnAlBr}_4 \cdots 5\text{C}_6\text{H}_6$	3.75	0	40
" $\text{I}_2\text{Sn}:\text{BCp}_2\text{I}$ "	4.03	0	40
$(\text{Me}_3\text{SnC}_5\text{H}_4)_2\text{Sn}$	3.58	0.89	
	1.30	0	53
$\text{Cp}_2\text{Sn}(\text{tcne})$	3.03	2.37	42
$\text{Cp}_2\text{Sn}(\text{tcne})_2$	3.12	2.26	42
$\text{Cp}_2\text{Sn}(\text{tcnq})$	3.84	1.30	42
$(\text{Me}_4\text{Sb})_2\text{SnCp}_4$	3.93	0.52	54
$\text{C}_6\text{H}_6\text{Sn}(\text{AlCl}_4)_2\text{C}_6\text{H}_6$	3.93	0	27

that all the π -bonded derivatives described in this section meet that criterion. The formation of adducts between stannocene and simple Lewis acids does not significantly change the s electron density of the tin atom. Also of note is the dramatic decrease in the IS of stannocene upon formation of polystannocene.

III

σ -BONDED COMPOUNDS

A. Structure

As mentioned in the introduction, the simple alkyl and aryl stannylenes originally formulated as R_2Sn are actually linear, branched, or cyclic polystannanes. One isomer of the compound "diphenyltin" is the cyclic hexamer dodecaphenyl cyclohexastannane as shown by its X-ray crystallographic structure determination (62).

The carborane derivatives $MC_2B_9H_{11}$ ($M = Ge, Sn, Pb$) (63), and bis(2-phenyl-1,2-dicarba-*closo*-dodecaborane(12-1-yl)tin(II) (64) were the first bona fide divalent derivatives of tin and lead containing σ -bonds to carbon. The proposed structures for the former compounds are shown in Fig. 7.

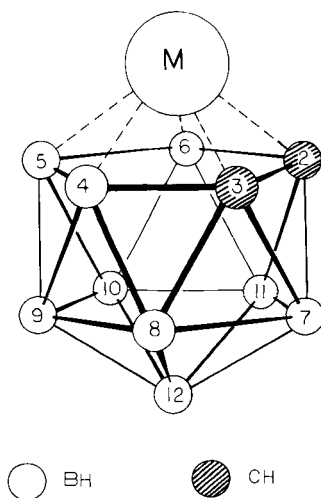


FIG. 7. Proposed structure of 1-germa-, 1-stanna-, and 1-plumba-2,3-dicarba-*closo*-dodecaborane(11) (63). Reprinted with permission from *J. Am. Chem. Soc.* **92**, 3351 (1972). Copyright by the American Chemical Society.

The bistrimethylsilylmethyl ligand has been utilized by Lappert and co-workers to stabilize a number of unusual valence states for lanthanide and transition metals (65–67). In group IV the bis(bistrimethylsilylmethyl)-germanium(II), tin(II), and lead(II) compounds have all been synthesized and the germanium and tin compounds shown to be monomeric in cyclohexane solution (68, 69).

The crystal structure of $\text{Sn}(\text{CH}(\text{SiMe}_3)_2)$ (see Fig. 8), however, shows this interesting compound to be a centrosymmetric dimer (69). In fact the Sn—Sn distance of 2.765 Å is close to that in hexaphenylditin (2.77 Å) (70). Since the solid is diamagnetic, a conventional tin–tin single bond is ruled out. Lappert has suggested that the tin–tin interaction be described as a “bent double bond” with the lone pair on each tin being donated into the empty orbital on the adjacent tin atom, as shown in Fig. 9.

The controversy over the degree of association of the isoelectronic stannylamine $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ has been resolved. Schaeffer and Zuckerman reported this compound to be dimeric in solution and in the vapor phase (71), while Harris and Lappert reported it to be monomeric (28, 72, 73). In a recent publication, Cowan and Zuckerman report that they find the compound to be monomeric and suggest that the earlier sample found to be dimeric may have been partially hydrolyzed (74).

An electron-diffraction study (75) of the vapor of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ has shown the N—Sn—N angle to be 96° , much closer to the Cl—Sn—Cl

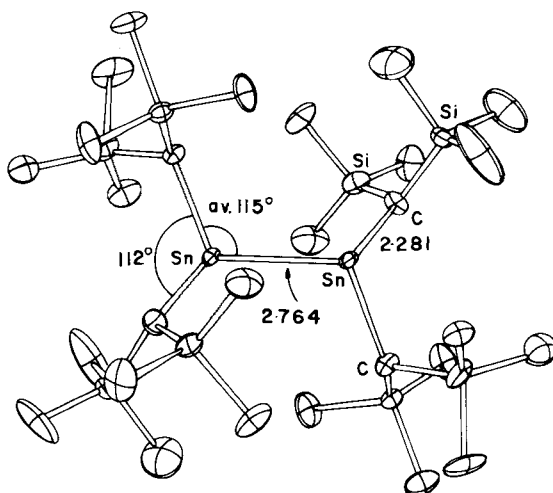


FIG. 8. Crystal structure of bis(bistrimethylsilylmethyl)tin(II) (69). Reprinted with permission from *J. Chem. Soc., Chem Commun.* p. 261 (1976). Copyright by The Chemical Society.

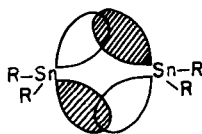


FIG. 9. Bent tin-tin double bond (68). Reprinted with permission from *J. Chem. Soc., Dalton Trans.* p. 2268 (1976). Copyright by The Chemical Society.

angle of 95° in the gas phase of stannous chloride (76) than to the Cp-Sn-Cp angle of 125° reported for the gas phase of stannocene (16).

B. Synthesis

As in synthesis of π -bonded divalent compounds, the principal method of synthesis is nucleophilic displacement of halogen from the divalent metal halide as shown in Eq. (34).

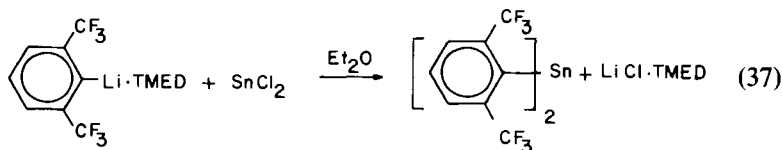
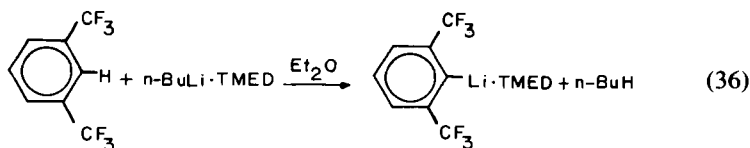


Synthesis of the corresponding germanium derivative was unsuccessful using GeCl_2 as a starting material; however, use of $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ yielded the analogous bis(bis(trimethylsilyl)methyl)germanium(II) (68).

The previously mentioned carbametallic boranes were also synthesized by nucleophilic displacement (63) as shown in Eq. (35).

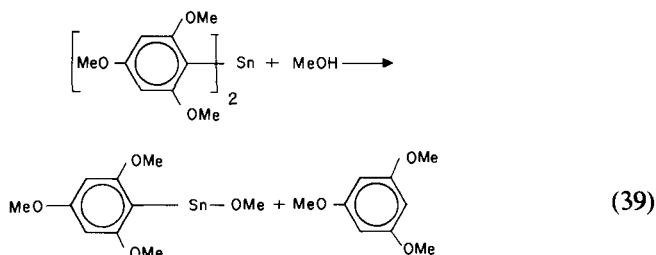
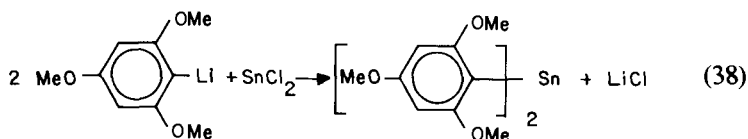


Salt elimination was also utilized in Eq. (37) to yield the first stable divalent aryl stannylene (77). The stability of the compound is attributed to the 2,6-substituents protecting the tin from nucleophilic attack. Similar at-



tempts with the corresponding methoxy-substituted arene gave a product which oligomerized on attempted recrystallization, but which, on treat-

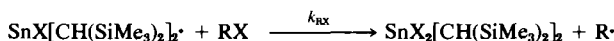
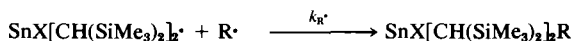
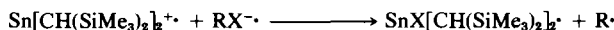
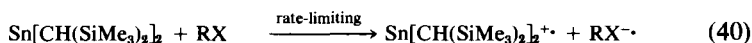
ment with methanol, gave the isolable aryl alkoxy stannylene shown in Eqs. (38) and (39).



C. Reactions

Early attempts at producing dialkyltin compounds yielded polymers. More recently, Neumann has found several synthetic routes to reactive " R_2Sn " intermediates which can be trapped by oxidative-addition reactions (3). In the absence of trapping agents the divalent tin compound polymerizes. Lappert and co-workers have shown that the bulky bistrimethylsilylmethyl ligand stabilizes the divalent tin species toward polymerization. This stable divalent tin species thus provides an excellent starting material for investigating a wide variety of oxidative-addition reactions, as shown in Fig. 10 (78).

Mechanistic studies have been carried out on the oxidative addition of alkyl halides to $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ (79, 80). Radical intermediates were observed by spin trapping, and when an optically active alkyl halide was used racemization occurred. The evidence obtained led to the proposed mechanism shown in Eq. (40).



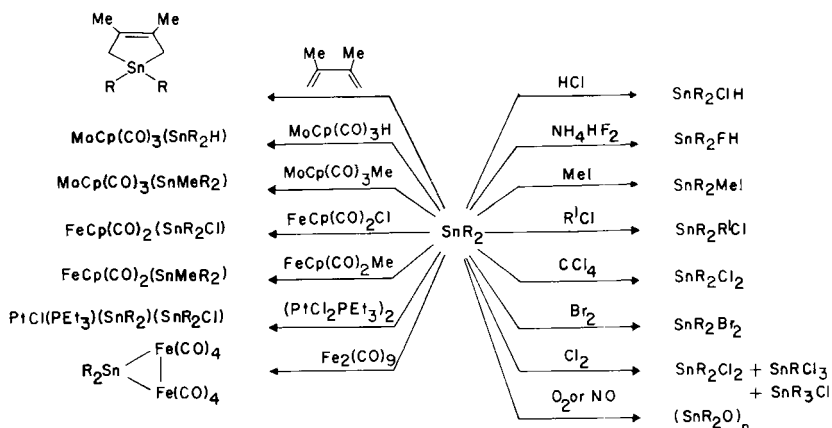
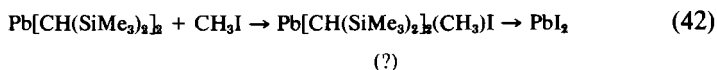


FIG. 10. Oxidative addition reactions of SnR_2 , $\text{R} = \text{CH}(\text{SiMe}_3)_2$ (78). Reprinted with permission from *J. Chem. Soc., Dalton Trans.* p. 2275 (1976). Copyright by The Chemical Society.

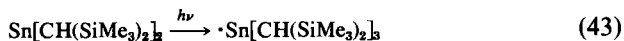
It has recently been reported that addition of a catalytic amount of ethyl bromide increases the rate of reaction of aryl halides with $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$, supportive of a radical mechanism (81).

Attempted oxidative addition reactions involving $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$ did not yield stable tetravalent products as shown in Eq. (41) and (42) (78). Reaction with methyl iodide shown in Eq. (42) resulted in rapid disappearance of the purple color due to $\text{Pb}[\text{CH}(\text{SiMe}_3)_2]_2$ followed by slow precipitation of PbI_2 .



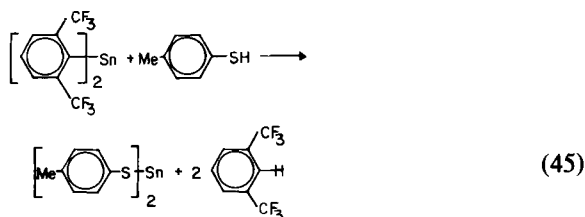
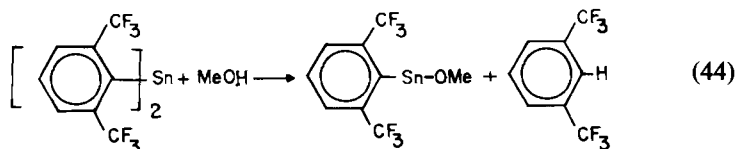
Unlike stannocene, $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ does not form adducts with main group Lewis acids such as BF_3 , but it does coordinate to transition metal complexes, as will be discussed in Section IV. Reactions with Lewis bases such as pyridine result in the formation of adducts at low temperature, but the compounds are unstable, decomposing upon warming to the starting materials (78).

Photolysis of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ yields the long-lived trivalent tin-centered radical shown in Eq. (43) (82, 83).

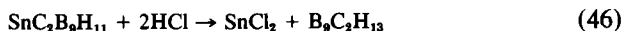


The ESR spectrum of this and related compounds is discussed in Section III, D. Attempted formation of the analogous lead radical led to formation of metallic lead.

Protolytic cleavage of bis(1,6-bis(trifluoromethyl)phenyl)tin(II) by methanol and *p*-toluenethiol (77), shown in Eqs. (44) and (45), are reminiscent of the reactions of stannocene shown in Eq. (24).



The carborane derivative 1-stanna-2,3-dicarba-*closo*-dodecaborane(II) is cleaved by hydrogen chloride (63) to give tin(II) chloride as shown in Eq. (46).



D. Spectroscopic Properties

Vibrational (IR and Raman), UV-visible, photoelectron, NMR, and Mössbauer spectroscopy have all been reported for bis(bis(trimethylsilyl)methyl)tin(II) and analogous tin(II) amides. Since an unusual tin-tin double bond has been proposed for the solid state of $[\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2]_2$ the Raman spectrum of this compound was of interest. Unfortunately, the compound decomposed in the laser beam; however, an intense band at 300 cm^{-1} has been assigned as the Ge-Ge stretching frequency for the analogous germanium compound (68).

The UV-visible spectra of a number of divalent group IV alkyls and amides have been collected (68, 72); however, the electronic transitions responsible for these bands have not yet been assigned. Listed in Table III are some qualitative observations on the color of the divalent alkyls $\text{M}[\text{CH}(\text{SiMe}_3)_2]_2$.

It is known that $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ is a monomer in solution and a dimer in the solid state. It is tempting to suggest that a monomer-dimer equilibrium is responsible for the thermochromicity described in Table III, but

TABLE III
COLORS AND SPECTROSCOPIC DATA OF DIVALENT GROUP IV ALKYL
UNDER VARIOUS CONDITIONS

State	Color		
	GeR ₂	SnR ₂	PbR ₂
Crystals at 20°C	Bright yellow	Brick red	Purple
Solution in hexane	Yellow	Deep magenta	—
Melt	Orange-red	Very deep red	—
At -196°C	Colorless	Pale yellow	Colorless
λ_{\max}^a			
	414 (970) ^a	495 (610)	
	302 (1450)	332 (910)	
	227 (19600)	239 (32750)	

^a λ_{\max} in hexane solution (extinction coefficients in parentheses).

such a conclusion awaits a more detailed study. The divalent amides are also thermochromic (72), and Zuckerman and Corvan have suggested that monomeric amides can be distinguished from associated amides on the basis of color (74). The UV photoelectron spectra of bis(bis(trimethylsilyl)methyl germanium, tin, and lead as well as their isoelectronic bis(bis(trimethylsilyl)amide analogs have been reported (84). The portion of each spectrum attributed to the lone pair metal electrons is listed in Table IV. In each case there is the expected decrease in ionization potential from germanium to lead. In the case of the bis-alkyl the low ionization potential correlates well with the known Lewis basicity of these compounds. The

TABLE IV
METAL LONE PAIR VERTICAL IONIZATION
POTENTIALS FOR DIVALENT METAL
ALKYLS AND AMIDES

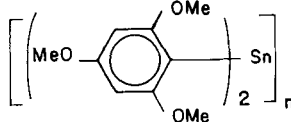
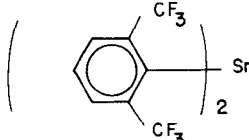
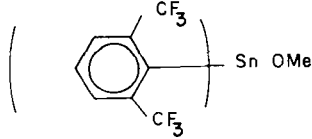
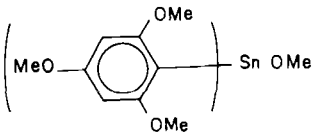
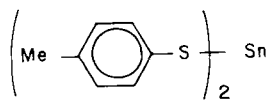
Compound ^a	IP (eV)
GeR ₂	7.75
SnR ₂	7.42
PbR ₂	7.25
Ge(NR ₂) ₂	8.68
Sn(NR ₂) ₂	8.38
Pb(NR ₂) ₂	8.16

^a R = CH(SiMe₃)₂, R¹ = SiMe₃.

nitrogen lone pair ionization potentials of the divalent silyl arides have been interpreted on the basis of Si—N π -bonding (85).

Lappert and co-workers have extensively studied the ESR spectra of the trivalent group IV radicals $M[N(SiMe_3)_2]_3\cdot$, and $M[CH(SiMe_3)_2]_3\cdot$ ($M = Ge, Sn$) (82, 83, 85–87). On the basis of increased ^{73}Ge and $^{117,119}Sn$

TABLE V
MÖSSBAUER DATA FOR σ -BONDED ORGANOSTANNYLENES

Compound	IS	QS	Reference
$SnCH(SiMe_3)_2$	2.16	2.31	88
$Sn[N(SiMe_3)_2]_3$	2.78	3.11	72
$Sn[N(SiMe_3)_2]_3NC_5H_5$	2.77	2.78	74
3-Sn-1,2- $B_6C_2H_{11}$	4.67	3.83	89
$Sn(C_6H_5CB_{10}H_{10}C)_2$	2.95	1.90	64
	1.60	0	77
	3.37	1.93	77
	2.88	2.31	77
	2.76	2.41	77
	3.48	1.79	77

hyperfine coupling it was concluded that the amide radicals are pyramidal whereas the alkyl radicals are approximately planar.

The Mössbauer data for a number of sigma bonded divalent tin compounds are collected in Table V (64, 72, 74, 77, 88, 89). The reader is referred to reference 74 for a more complete list of divalent amides; we have listed here only $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ for comparison to the isoelectronic alkyl compound. The exceptionally low value for the divalent compound $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ is no doubt due to its unusual dimeric structure in the solid state. All the other compounds listed in Table V as divalent structures have isomer shifts above the often-used dividing line of 2.56 mm/sec for tin(II).

IV

TRANSITION METAL COMPLEXES

A. Structure

Organic compounds of divalent tin and lead form a variety of transition metal complexes. On the basis of the structure of the group IV ligand, these can be classified as either terminal, base-stabilized terminal, or bridging. The bonding in terminal complexes can be interpreted as involving σ -donation from the lone pair of the group IV donor to the transition metal and back donation from the transition metal to empty p or d orbitals on the group IV ligand. This is similar to the bonding in the well-known carbene complexes (90, 91). Base stabilized terminal complexes involve coordination of the group IV ligand to only one metal, but the vacant p orbital on the group IV ligand additionally coordinates a mole of base. Bridging complexes contain formally divalent group IV ligands linking two transition metals.

The structure of the terminal stannylene complex $[\text{CH}(\text{SiMe}_3)_2]_2\text{-SnCr}(\text{CO})_5$ is shown in Fig. 11 (92). Significant in this structure is the coplanarity of the C1, Sn, C2, and Cr atoms. This and spectroscopic evidence (see Section IV,D) indicate back donation from the transition metal to the stannylene ligand. The relatively short Sn—Cr bond length of 2.562 Å compares to 2.654 Å for the base-stabilized complex $t\text{-Bu}_2\text{Sn}(\text{py})\text{SnCr}(\text{CO})_5$ (see Fig. 12) (93) and 2.85 Å for the tetravalent complex $\text{Ph}_3\text{SnCr}(\text{CO})_3\text{Cp}$ (94). The structure for the analogous germylene complex $[\text{CH}(\text{SiMe}_3)_2]_2\text{GeCr}(\text{CO})_5$ has been determined, and it is quite similar to the stannylene complex (95). On the basis of infrared data, the

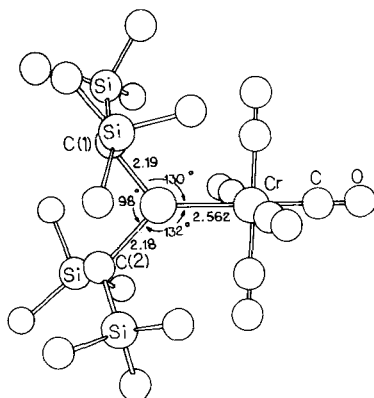


FIG. 11. Crystal structure of $(\text{CH}(\text{SiMe}_3)_2)_2\text{SnCr}(\text{CO})_5$ (92). Reprinted with permission from *J. Chem. Soc., Chem. Commun.* p. 893 (1974). Copyright by The Chemical Society.

cyclopentadienyl rings in the terminal stannylenes complexes $\text{Cp}_2\text{SnM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) are pentahapto (52). A structure similar to that shown in Fig. 11 has been proposed for these complexes.

The X-ray crystallographic structure of the base stabilized terminal stannylenes complex $t\text{-Bu}_2\text{Sn}(\text{py})\text{Cr}(\text{CO})_5$ is shown in Fig. 12 (93). The slightly longer $\text{Sn}-\text{Cr}$ bond length in this complex, and the slight eleva-

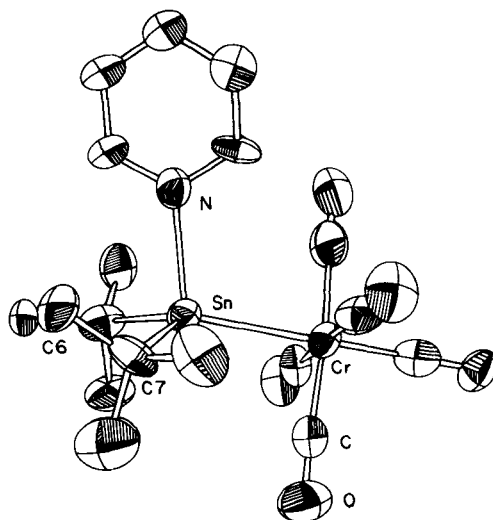


FIG. 12. Crystal structure of $\text{Sn-}t\text{-Bu}_2(\text{py})\text{Cr}(\text{CO})_5$ (93). Reprinted with permission from *J. Am. Chem. Soc.* **95**, 4529 (1973). Copyright by the American Chemical Society.

tion of the Sn atom above the Cr,C6,C7 plane may indicate less back donation from the transition metal when the vacant p orbital on the stannylene coordinates to base.

A number of base-stabilized iron tetracarbonyl complexes of the form $R_2M(B)Fe(CO)_4$, presumably with structures related to that shown in Fig. 12, have been synthesized or shown to exist in solution (see Section IV,C). Removal of the coordinated base yields the bridging complexes $[R_2MFe(CO)_4]_2$. The structure of the stannocene bridged complex $[Cp_2SnFe(CO)_4]_2$ is shown in Fig. 13 (96). The bond lengths and angles in the Fe_2Sn_2 ring are identical (within 1%) to the corresponding values of the analogous $[Me_2SnFe(CO)_4]_2$ (97). The planarity of the monohapto cyclopentadienyl rings is interesting in this compound. The cyclopentadienyl rings of the related compound $Cp_2Sn[Fe(CO)_2Cp]_2$ are puckered (98); however, the crystal structure of 1,1-bis(trimethylstannyl)cyclopentadiene has been determined (99), and the cyclopentadiene ring found to be planar.

B. Synthesis

Organostannylene and plumbylene complexes of transition metals can be synthesized from both divalent and tetravalent starting materials.

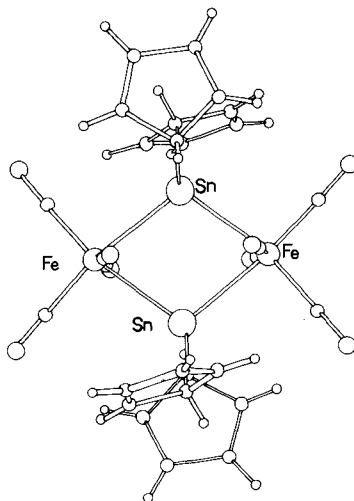
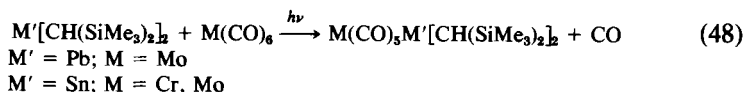
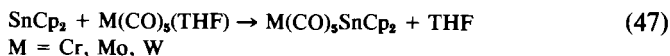


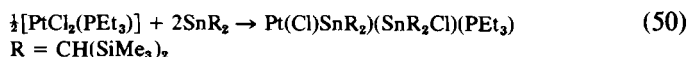
FIG. 13. Crystal structure of $(Cp_2SnFe(CO)_4)_2$ (96). Reprinted with permission from *J. Chem. Soc., Dalton Trans.* p. 2097 (1975). Copyright by The Chemical Society.

When the divalent compound is stable, the complexes are synthesized by ligand displacement reactions such as those shown in Eqs. (47) (52), (48) (78, 100), and 49 (78).



The reaction of $[\text{Fe}(\text{CO})_2\text{Cp}]_2$ and $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ in refluxing hexane yields $\text{Fe}_2(\text{CO})_3\text{Cp}_2[\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2]$. The stannylene ligand was determined to be terminally bound on the basis of the infrared spectrum of the complex (78). Reaction of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ and $\text{Mo}(\text{CO})_4$ (norbornadiene) resulted in displacement of norbornadiene to give the trans bis-substituted stannylene complex. No evidence was obtained for the cis isomer, probably because of the bulky nature of the stannylene ligand (78).

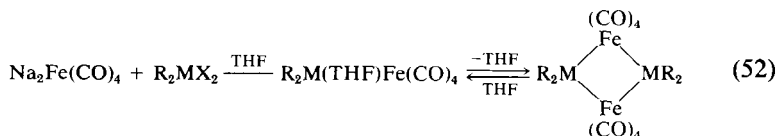
In addition to serving as ligands, organostannylenes can also insert into metal-ligand bonds (cf. Fig. 10). In the reaction shown in Eq. (50) (78), two moles of the divalent tin compound react, one forming a terminal stannylene complex, and the other inserting into the Pt—Cl bond.



Base-stabilized organostannylene complexes can be synthesized as shown in Eq. (51) by reduction of tetravalent organotin dihalides (101).



Attempts to synthesize the chromium compounds in the absence of coordinating solvents were unsuccessful, and attempts to remove the base led to decomposition. Similar reactions with disodium tetracarbonyl ferrate gave the base-stabilized iron tetracarbonyl compounds shown in Eq. (52). Removal of the coordinated base gave the bridging structure shown (102).



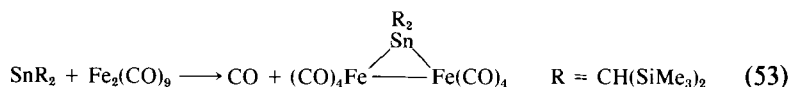
$\text{M} = \text{Ge}, \text{R} = \text{C}_6\text{H}_5, \text{CH}_3$

$\text{M} = \text{Sn}, \text{R} = \text{C}_6\text{H}_5, \text{CH}_3, t\text{-C}_4\text{H}_9$

$\text{M} = \text{Pb}, \text{R} = \text{C}_6\text{H}_5, n\text{-C}_4\text{H}_9$

Such cyclic structures are available by a wide variety of metal-metal bond forming reactions (103-105).

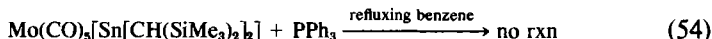
Stannocene reacts with $\text{Fe}_2(\text{CO})_9$ to give the bridging stannylene complex $[\text{SnCp}_2\text{Fe}(\text{CO})_4]_2$, the structure of which was shown in Fig. 13. Bis(bis(trimethylsilyl)methyl)tin(II) does not react analogously, giving instead the complex shown in Eq. (53).



The complex showed no bridging carbonyl bands in the infrared, and is assumed to have the three-membered ring structure shown (78).

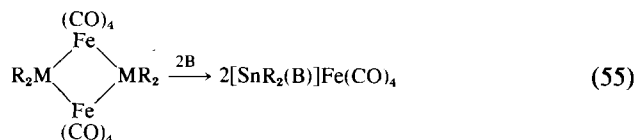
C. Reactions

Very few reactions have been reported for organostannylene and plumbylene complexes. The complexes are generally air sensitive, but less so than the parent divalent stannylenes or plumbylenes. Triphenylphosphine fails to displace the terminal stannylene in the complex shown in Eq. (54).



This indicates that the stannylene ligand is strongly held. Additionally, attempts at coordinating other bases to the "vacant" orbital of the stannylene failed with this and related complexes of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ (78). That is noteworthy, since analogous dialkylstannylene-chromiumpenta-carbonyl complexes with smaller alkyl groups attached to the tin are unstable in the absence of coordinated base (101).

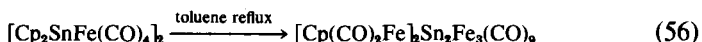
As mentioned earlier, the bridging complexes $[\text{R}_2\text{MFe}(\text{CO})_4]_2$ are cleaved by base, as shown in Eq. (55).



The extent of base cleavage could be qualitatively estimated from changes in the infrared spectra (102). Increasing dissociation was found to follow the order of increasing base strength, viz., diethyl ether < THF < acetone < pyridine. The pyridine complexes $t\text{-Bu}_2\text{Sn}(\text{py})\text{Fe}(\text{CO})_4$ and $\text{Me}_2\text{Ge}(\text{py})\text{Fe}(\text{CO})_4$ could be isolated, but attempts at isolating other base-

stabilized complexes resulted in loss of coordinated base and regeneration of the bridged structure. Similar behavior was observed for the stannylene complex $[\text{SnCp}_2\text{Fe}(\text{CO})_4]_2$ (52).

The bridging stannylene complex $[\text{Cp}_2\text{SnFe}(\text{CO})_4]_2$ undergoes the thermal rearrangement shown in Eq. (56) in which the σ -bonded cyclopentadienyl group is transferred from tin to the transition metal.



The novel cluster compound formed in this reaction involves two tin atoms bound terminally to the two $[\text{Fe}(\text{CO})_2\text{Cp}]$ groups, and bound to opposite faces of the triangular $\text{Fe}_3(\text{CO})_9$ cluster (106). The transfer of σ -bound, monohapto cyclopentadienyl groups from tin to a transition metal has considerable precedent (107, 108).

D. Spectroscopic Properties

Since tin is both donating and accepting electron density in the base-stabilized terminal complexes, there has been some question about the correct designation of its oxidation state. Mössbauer data and photoelectron spectroscopic data have been reported for the complexes $t\text{-Bu}_2\text{Sn}(\text{B})\text{Fe}(\text{CO})_4$ and $t\text{-Bu}_2\text{Sn}(\text{B})\text{Cr}(\text{CO})_5$ ($\text{B} = \text{THF}, \text{DMSO}, \text{py}$) (109). These data were interpreted as being more indicative of a tin(IV) rather than a tin(II) oxidation state. Formal oxidation states are only useful as electron counting devices when electron delocalization becomes extensive as it apparently is in these interesting compounds.

Tin-119 Mössbauer data have been reported for a number of stannylene complexes and are collected in Table VI. The IS (isomer shift) of the stannocene complexes is much lower than that of stannocene, while the QS (quadrupole splitting) is much higher. This has been interpreted as indicating synergistic σ - plus π -bonding of the stannylene to the transition metal (52).

There is little change in the IS values of tin on complexation of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ to transition metals, but it must be remembered that the "free" ligand is a dimer (88). There is a dramatic increase in the QS values upon coordination of $\text{Sn}[\text{CH}(\text{SiMe}_3)_2]_2$ to a transition metal, possibly reflecting back donation from the transition metal to empty orbitals on the stannylene.

Iron-57 Mössbauer data have been reported for the complexes $[\text{Cp}_2\text{SnFe}(\text{CO})_4]_2$ and $\text{Cp}_2\text{Sn}(\text{py})\text{Fe}(\text{CO})_4$. The IS values are similar to those for the $\text{LFe}(\text{CO})_4$ complexes, $\text{L} = \text{Co}, \text{PPh}_3, \text{P}(\text{OEt})_3$, and on this

TABLE VI
 TIN-119 MÖSSBAUER DATA FOR TRANSITION METAL STANNYLENE COMPLEXES

Compound	IS	QS	Reference
Terminal stannylenes			
$\text{Cr}(\text{CO})_5\text{SnR}_2^a$	2.21	4.43	88
$\text{Mo}(\text{CO})_5\text{SnR}_2^a$	2.15	4.57	88
<i>trans</i> - $\text{Cr}(\text{CO})_4(\text{SnR}_2)_2^a$	2.21	4.40	88
$\text{PtCl}(\text{PEt}_3)(\text{SnR}_2)(\text{SnR}_2\text{Cl})^a$	2.05	4.23	88
	1.73	2.66	88
$\text{Cp}_2\text{SnCr}(\text{CO})_5$	1.86	2.60	52
$(\text{MeCp})_2\text{SnCr}(\text{CO})_5$	1.92	2.51	52
$\text{Cp}_2\text{SnMo}(\text{CO})_5$	1.96	2.71	52
$(\text{MeCp})_2\text{SnMo}(\text{CO})_5$	2.00	3.13	52
$(\text{MeCp})_2\text{W}(\text{CO})_5$	1.90	2.51	52
Base-stabilized terminal stannylenes			
$\text{Sn-}t\text{-Bu}_2(\text{THF})\text{Cr}(\text{CO})_5$	2.11	4.14	109
$\text{Sn-}t\text{-Bu}_2(\text{DMSO})\text{Cr}(\text{CO})_5$	1.98	3.60	109
$\text{Sn-}t\text{-Bu}_2(\text{py})\text{Cr}(\text{CO})_5$	2.01	3.44	109
$\text{Sn-}t\text{-Bu}_2(\text{py})\text{Fe}(\text{CO})_4$	1.82	3.06	109
$\text{Sn-}t\text{-Bu}_2(\text{DMSO})\text{Fe}(\text{CO})_4$	1.90	3.60	109
Bridging stannylenes			
$(\text{Fe}(\text{CO})_4)_2\text{SnR}_2^a$	1.73	1.53	88
$(t\text{-Bu})_2\text{SnFe}(\text{CO})_4)_2$	1.83	1.16	109
$(\text{Cp}_2\text{SnFe}(\text{CO})_4)_2$	1.86	0	52
$(\text{MeCp}_2\text{SnFe}(\text{CO})_4)_2$	1.81	0	52
$(\text{MeCp}_2\text{SnFe}(\text{CO})_4)_2$ pyridine solution	1.45	1.89	52

^a $\text{R} = \text{CH}(\text{SiMe}_3)_2$.

basis it was concluded that the stannylene ligand has similar strength as a σ -donor (52).

As mentioned earlier, the infrared spectra of the complexes $\text{Cp}_2\text{SnM}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were used to show the pentahapto mode of bonding of the cyclopentadienyl group. On the basis of the infrared spectra of the carbonyl groups bound to the complexes $\text{R}_2\text{Sn}(\text{THF})\text{Cr}(\text{CO})_5$, $\text{R} = \text{Me}, t\text{-Bu}$, the base-stabilized organostannylene ligands were classified as strong σ -donors, and as π -acceptors at least as strong as carbenes (101).

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Novel Types of Metal–Metal Bonded Complexes Containing Allyl and Cyclopentadienyl Bridging Ligands

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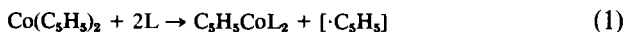
I

INTRODUCTION

Binuclear sandwich-type complexes possessing a metal–metal bonded M_2 unit coordinated by two planar C_nH_n ring systems are very rare. In 1965, Allegra *et al.* (1) reported the synthesis of the binuclear complex $(C_6H_6)_2Pd_2(Al_2Cl_7)_2$ in which two directly bonded palladium atoms are sandwiched by two benzene ligands. The same authors also prepared the similar compound $(C_6H_6)_2Pd_2(AlCl_4)_2$, which again shows a sandwich-type structure (2).

It seems most noteworthy that, despite the real progress made in the synthesis of various types of di- and polynuclear π -cyclopentadienylmetal complexes [see, e.g., the triple-decker and other multi-decker sandwiches (3, 4)], there was no report in the literature concerning $(\mu-C_5H_5)M_2$ complexes until 1975 when we described the synthesis of the compounds $(C_5H_5)(2-RC_3H_4)Pd_2L_2$, possessing a planar five-membered ring bridging a linear $L-Pd-Pd-L$ fragment (5). The discovery of this new type of cyclopentadienylmetal complex was not straightforward but followed from our interest in ring ligand displacement reactions of sandwich-like molecules (6).

Among dicyclopentadienylmetal species, cobaltocene and nickelocene were known to react under rather mild conditions with various Lewis bases L [e.g., CO, PF₃, PPh₃, P(OR)₃] to give the 18-electron complexes C₅H₅CoL₂ and NiL₄, respectively (6).



We thought it important to learn how these ring ligand displacement reactions occur, and thus we investigated the kinetics of these processes (7). Due to some difficulties in interpreting the kinetic data of Eq. (2), we included in our studies the π -allyl- π -cyclopentadienylmetal complexes C₅H₅M(all),¹ where M is Ni and Pd (8). These complexes, which are similar in structure to Ni(C₅H₅)₂, also react with monodentate ligands L to give ML₄ compounds. In contrast to nickelocene, they have the advantage of being diamagnetic, and therefore the course of their reactions with L can be followed by NMR spectroscopy.

From these studies, mainly performed with the palladium complexes C₅H₅Pd(all) as starting materials (all = C₃H₅, 2-MeC₃H₄, 2-*t*-BuC₃H₄, 1,1,2-Me₃C₃H₂), the following mechanistic picture emerged (8, 9):



Attack of Lewis base L on the starting compound gives C₅H₅Pd(all)L as the primary intermediate, which possesses either a π -bonded cyclopentadienyl and a σ -bonded allyl, or a π -bonded allyl and a σ -bonded cyclopentadienyl group. For L = P(OR)₃, the first possibility could be confirmed by NMR measurements (9). During the course of the work, we found not only that the stability of the intermediate C₅H₅Pd(all)L strongly depends on the type of ligand L, but also—and more surprisingly—that under different conditions the complexes C₅H₅Pd(all) react with stoichiometric amounts of L to give not mononuclear complexes but binuclear compounds of the composition (C₅H₅)(all)Pd₂L₂ (5). X-Ray structure investigations proved that they have a sandwich-type structure, i.e., the two organic ligands coordinate not one metal atom but an M₂ unit (5, 10).

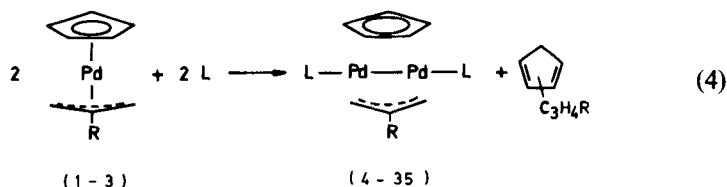
The ease of quantitative formation of these products prompted us (1) to investigate in more detail the mechanism, bonding, and reactivity of this new class of organometallic complexes and (2) to elucidate whether other metals and other types of ligands may form analogous binuclear compounds.

¹ Throughout this article, "all" represents an allyl group.

II

THE ORIGINAL SYNTHETIC PATHWAY

The original synthesis of the binuclear complexes $(C_5H_5)(all)Pd_2L_2$ according to Eq. (4) can be performed with various phosphines, phosphites, and arsines as ligands (10, 11). Benzene and toluene are the preferred solvents. In most cases the reaction is quite rapid at room temperature, leading to complete formation of the products in a very few minutes. Higher temperatures are only necessary with bulky ligands such as $P-i-Pr_3$ or PCy_3 ($Cy = cyclo-C_6H_{11}$). The importance of steric effects is also evident from a comparison of the reaction rate of the three starting complexes **1**, **2**, and **3** with $P-i-Pr_3$. Whereas **1** reacts nearly instantaneously with the phosphine at room temperature to give **5**, the reaction of **2** with $P-i-Pr_3$ to give **12** takes 1 h at 25°C, and that of **3** with $P-i-Pr_3$ to give **27** proceeds only at 90°C.



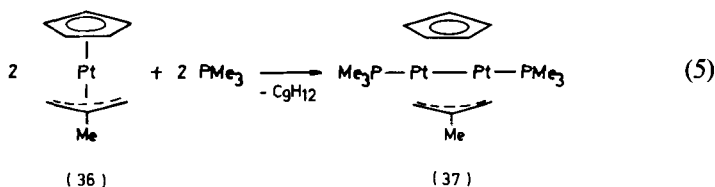
L	R			L	R		
	H	Me	<i>t</i> -Bu		H	Me	<i>t</i> -Bu
PPh_3	(4)	(8)	(24)	PCy_3		(16)	
PPh_2Me		(9)	(25)	$PPhCy_2$		(17)	(31)
$PPhMe_2$		(10)	(26)	$P(OMe)_3$		(18)	(32)
PMe_3		(11)		$P(O-i-Pr)_3$		(19)	
$P-i-Pr_3$	(5)	(12)	(27)	$P(OPh)_3$		(20)	(33)
PBu_3		(13)	(28)	$P(OC_6H_4-o-Me)_3$		(21)	(34)
$P-i-Bu_3$		(14)	(29)	$As-i-Pr_3$	(6)	(22)	(35)
PPh_2-t-Bu		(15)	(30)	$As(CH_2Ph)_3$	(7)	(23)	

The most bulky phosphine $P-t-Bu_3$ does not produce a binuclear compound at all on reaction with **1**, **2**, or **3**. Under various conditions, the only product is $Pd(P-t-Bu_3)_2$. This complex, first described by Otsuka *et al.* (12), is particularly inert toward $C_5H_5Pd(all)$, although the metal has only a 14-electron configuration. The sterically demanding $P-t-Bu_2Ph$ behaves

similarly; i.e., it forms $\text{Pd}(\text{P-}t\text{-Bu}_2\text{Ph})_2$ on reaction with **2**, whereas $\text{P-}t\text{-BuPh}_2$ gives $(\text{C}_5\text{H}_5)(2\text{-RC}_3\text{H}_4)\text{Pd}_2(\text{P-}t\text{-BuPh}_2)_2$ (**15**, **30**) (11).

Experiments aimed at the synthesis of binuclear (Ni—Ni) complexes of the type $(\text{C}_5\text{H}_5)(\text{all})\text{Ni}_2\text{L}_2$ failed. Both $\text{C}_5\text{H}_5\text{NiC}_3\text{H}_5$ and $\text{C}_5\text{H}_5\text{Ni}(2\text{-MeC}_3\text{H}_4)$ are much more inert toward tertiary phosphines and phosphites than the corresponding palladium complexes **1** and **2** and react at higher temperatures, e.g., with PPh_3 or P(Ph)_3 , to give NiL_4 (11).

The compound $\text{C}_5\text{H}_5\text{Pt}(2\text{-MeC}_3\text{H}_4)$ (**36**) seems to be intermediate in reactivity between $\text{C}_5\text{H}_5\text{Pd}(2\text{-MeC}_3\text{H}_4)$ (**2**) and $\text{C}_5\text{H}_5\text{Ni}(2\text{-MeC}_3\text{H}_4)$. With PMe_3 in benzene it forms $(\text{C}_5\text{H}_5)(2\text{-MeC}_3\text{H}_4)\text{Pt}_2(\text{PMe}_3)_2$ (**37**) in good yields, according to Eq. (5) (11).



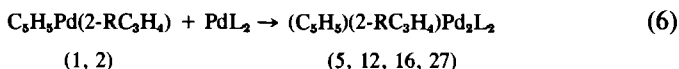
Some other tertiary phosphines react similarly and give the binuclear complexes $(\text{C}_5\text{H}_5)(\text{all})\text{Pt}_2\text{L}_2$ together with $\text{C}_5\text{H}_5\text{Pt}(\text{all})\text{L}$. For $\text{all} = 2\text{-MeC}_3\text{H}_4$ and $\text{L} = \text{P-}i\text{-Pr}_3$ or PCy_3 , these mononuclear compounds have been isolated and structurally characterized (13). On heating, they react to give $(\text{C}_5\text{H}_5)(2\text{-MeC}_3\text{H}_4)\text{Pt}_2(\text{PR}_3)_2$. This process is accompanied by partial decomposition and thus does not create a favorable synthetic pathway to yield the corresponding binuclear (Pt—Pt) complexes (11).

III

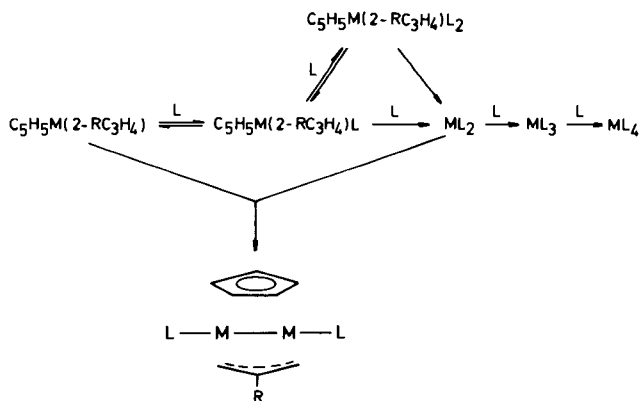
THE MORE ELEGANT ROUTE

Studies concerned with the problem of how the binuclear products of Eqs. (4) and (5) are formed led to an alternative synthetic route which proved to be of general importance. As already mentioned, the first step in the reaction of $\text{C}_5\text{H}_5\text{M}(\text{all})$ complexes with L (a donor molecule) undoubtedly involves formation of the mononuclear complexes $\text{C}_5\text{H}_5\text{M}(\text{all})\text{L}$, some of which for both Pd and Pt can be isolated and characterized (13, 14). These primary products react with a second molecule of L to give either directly ML_2 and $\text{C}_5\text{H}_5(\text{all})$ or a further intermediate $\text{C}_5\text{H}_5\text{M}(\text{all})\text{L}_2$ [e.g., for $\text{L} = \text{P(OR)}_3$ (9)] which in most cases is very short-lived and gives ML_2 by loss of allylcyclopentadiene. In the presence of L , the 14-electron complex ML_2 produces ML_3 or ML_4 (depending on the

The mechanistic proposal summarized by Scheme 1 (3) was first confirmed by the synthesis of compounds **5**, **12**, **16**, and **27** according to Eq. (6) (15).

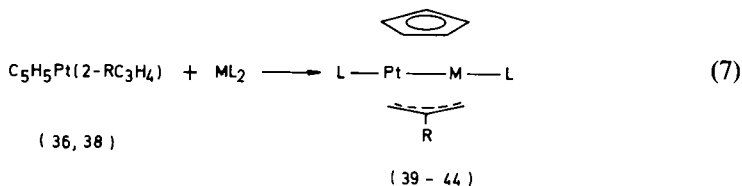


Whereas attempts to obtain (Ni–Ni) complexes $(C_5H_5)(2-RC_3H_4)Ni_2L_2$ by the alternative route, i.e., from $C_5H_5Ni(2-RC_3H_4)$ and $Ni(PPh_3)_n$ ($n = 2-3$) or $[(PCy_3)_2Ni]_2N_2$, again failed, the reaction of $C_5H_5Pt(2-RC_3H_4)$ (**36**, **38**) with $Pt(P\text{-}i\text{-}Pr)_2$ gives the (Pt–Pt) complexes **39** and **40** in



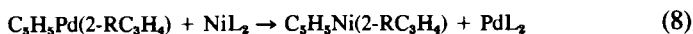
SCHEME 1

good yields (11, 15). Most noteworthy, the same starting materials (36, 38) also react with PdL_2 ($\text{L} = \text{P-}i\text{-Pr}_3$, PCy_3) to form binuclear products containing a palladium–platinum bond (18).

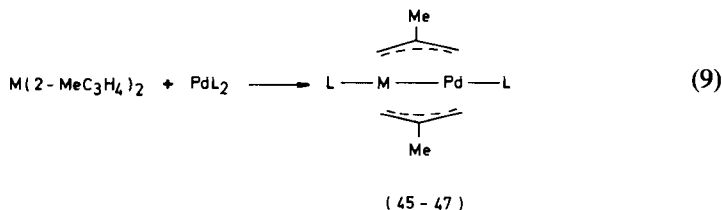


- (39) $\text{M} = \text{Pt}$, $\text{R} = \text{H}$, $\text{L} = \text{P-}i\text{-Pr}_3$
 (40) $\text{M} = \text{Pt}$, $\text{R} = \text{Me}$, $\text{L} = \text{P-}i\text{-Pr}_3$
 (41) $\text{M} = \text{Pd}$, $\text{R} = \text{H}$, $\text{L} = \text{P-}i\text{-Pr}_3$
 (42) $\text{M} = \text{Pd}$, $\text{R} = \text{Me}$, $\text{L} = \text{P-}i\text{-Pr}_3$
 (43) $\text{M} = \text{Pd}$, $\text{R} = \text{H}$, $\text{L} = \text{PCy}_3$
 (44) $\text{M} = \text{Pd}$, $\text{R} = \text{Me}$, $\text{L} = \text{PCy}_3$

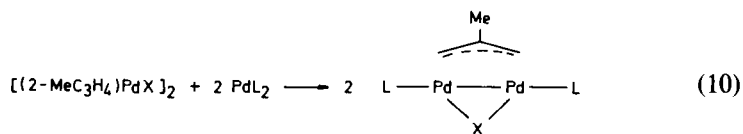
The heterometallic complexes 41–44 cannot be obtained from $\text{C}_5\text{H}_5\text{Pd}(2\text{-RC}_3\text{H}_4)$ and PtL_2 . In general, there seems to be a trend in reactivity of the 14-electron compounds ML_2 toward $\text{C}_5\text{H}_5\text{Pd}(2\text{-RC}_3\text{H}_4)$ following the order $\text{M} = \text{Pt} < \text{Pd} < \text{Ni}$ (11). $\text{Ni}(\text{PPh}_3)_n$ and $[(\text{PCy}_3)_2\text{Ni}]_2\text{N}_2$ (both sources of NiL_2) react rapidly with $\text{C}_5\text{H}_5\text{Pd}(2\text{-RC}_3\text{H}_4)$ not to form binuclear heterometallic complexes $(\text{C}_5\text{H}_5)(2\text{-RC}_3\text{H}_4)\text{NiPdL}_2$ ($\text{L} = \text{PPh}_3$, PCy_3) but to give $\text{C}_5\text{H}_5\text{Ni}(2\text{-RC}_3\text{H}_4)$ and PdL_2 [together with small amounts of $(\text{C}_5\text{H}_5)(2\text{-RC}_3\text{H}_4)\text{Pd}_2\text{L}_2$] (11).



The more elegant route—which we call for simplicity “the method of [1 + 1]-addition”—may also be used to prepare other binuclear complexes containing either two allyl groups, or one allyl group and one halogen in the bridging positions. The results so far obtained are summarized in Eqs. (9) and (10). Compounds 45–47 are the first allyl–transition metal complexes in which not one metal atom but a dimetal unit is coordinated sandwich-like by two η^3 -bonded allylic ligands (15, 19).



- (45) $\text{M} = \text{Pd}$, $\text{L} = \text{P-}i\text{-Pr}_3$
 (46) $\text{M} = \text{Pd}$, $\text{L} = \text{PCy}_3$
 (47) $\text{M} = \text{Pt}$, $\text{L} = \text{P-}i\text{-Pr}_3$



(48 - 51)

 (48) L = *P*-*i*-Pr₃, X = Cl

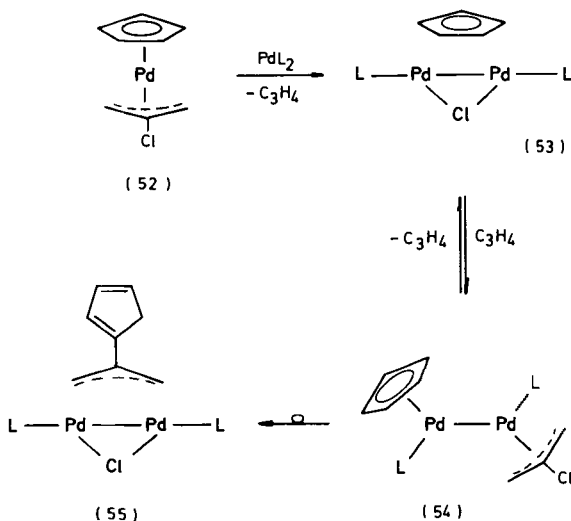
 (49) L = *P*-*i*-Pr₃, X = I

 (50) L = *P*-*t*-Bu₃, X = Cl

 (51) L = PCy₃, X = Cl

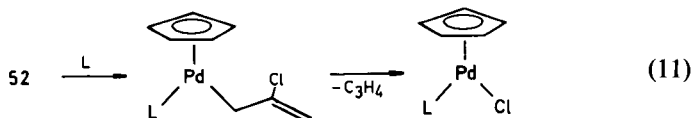
Compound Pd(*P*-*t*-Bu₃)₂, which is too inert to react with C₅H₅Pd(2-MeC₃H₄) or Pd(2-MeC₃H₄)₂ to give a binuclear product, reacts with [(2-MeC₃H₄)PdCl]₂ to form **50**. In this stable compound the two metal atoms are well protected by the bulky tri-*tert*-butylphosphine ligands.

The substituted μ -allyl complex (2-C₅H₅C₃H₄)(Cl)Pd₂(*P*-*i*-Pr₃)₂ (**55**) was unexpectedly obtained by the reaction sequence shown in Scheme 2 (11). The starting compound **52** reacts with PdL₂ (L = *P*-*i*-Pr₃) in benzene to give, possibly via (C₅H₅)(2-ClC₃H₄)Pd₂L₂ (**20**), a mixture of products in which (C₅H₅)(Cl)Pd₂L₂ (**53**) is the main component. By allowing the allene-containing solution to stand, the unsymmetrical nonbridged (Pd–Pd) complex **54** is formed whose structure is deduced from the ¹H-, and ³¹P-NMR spectra (11). Warming of a benzene solution of **54** leads to quantita-

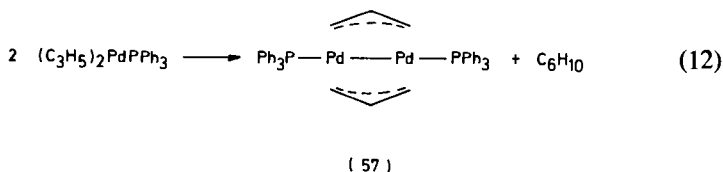


SCHEME 2

tive isomerization and formation of the μ -allyl complex **55**. The reaction of **52** with equimolar amounts of $L = PPh_3$, $P-i-Pr_3$, PCy_3 and $AsPh_3$ also does not yield a binuclear complex $(C_5H_5)(2-ClC_3H_4)Pd_2L_2$ but gives, by elimination of allene, the stable mononuclear products $C_5H_5Pd(L)Cl$ (**11**, **21**).



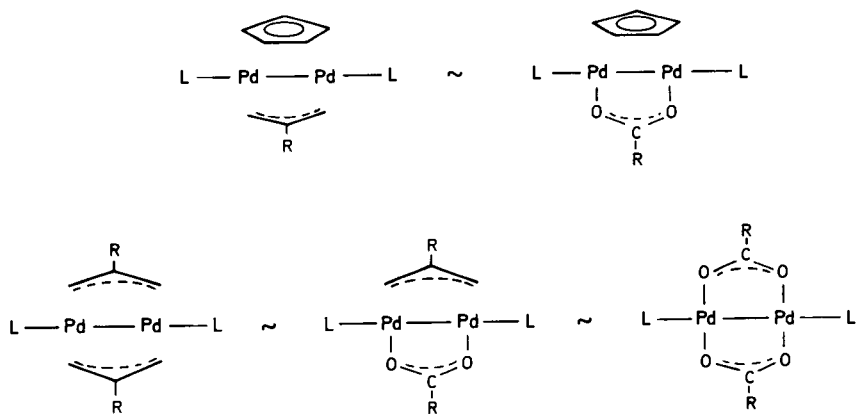
The synthesis of binuclear complexes of general composition $(all)(X)Pd_2L_2$ is obviously possible also by treating $[(all)PdX]_2$ with donor groups L . In 1972, Kobayashi *et al.* (22) described the preparation and structure of $(C_5H_5)(I)Pd_2(PPh_3)_2$ (**56**) obtained by the reaction of $[(C_5H_5)PdI]_2$ with triphenylphosphine. We were not successful in applying this method—which is analogous to our original method of preparing the compounds $(C_5H_5)(all)Pd_2L_2$ —to the synthesis of bis(μ -allyl) complexes $(all)_2M_2L_2$ ($M = Pd, Pt$). The starting materials $M(all)_2$ react readily with L to give mononuclear compounds $(\pi-all)M(\sigma-all)L$, some of which are fluxional in solution and show a π -allyl/ σ -allyl ligand exchange (23, 24). In contrast to our efforts, Jolly *et al.* succeeded in isolating complex $(C_5H_5)_2Pd_2(PPh_3)_2$ (**57**) formed according to Eq. (12) (25).



IV

THE SYNTHESIS OF CARBOXYLATE-BRIDGED (Pd-Pd) COMPLEXES

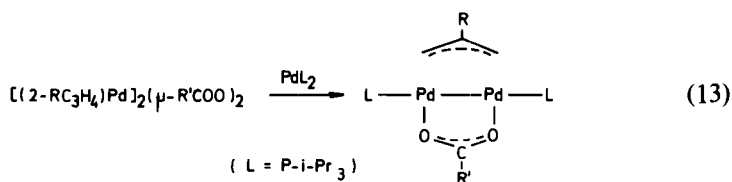
The stability of the 2-methylallyl complexes of general composition $(C_5H_5)(2-MeC_3H_4)Pd_2L_2$ and $(2-MeC_3H_4)_2Pd_2L_2$ posed the question of whether corresponding binuclear compounds containing one or two bridging acetate ligands instead of 2-methylallyl groups would be accessible. The two anionic species $MeCOO^-$ and $2-MeC_3H_4^-$ are isostructural and isoelectronic, each contributing four electrons when coordinated as bridging ligands. The difference, however, is that the acetate is not a π -donating ligand and thus should not be bonded in the same way as the 2-meth-



SCHEME 3

ylallyl group. The formal relationship between the binuclear allyl and carboxylate complexes is outlined in Scheme 3.

The preparation of the compounds $(2\text{-RC}_3\text{H}_4)(\text{MeCOO})\text{Pd}_2\text{L}_2$ was achieved by the reaction of the acetate-bridged palladium(II) complexes $[(2\text{-RC}_3\text{H}_4)\text{Pd}]_2(\mu\text{-MeCOO})_2$ with PdL_2 ($\text{L} = \text{P-}i\text{-Pr}_3$). The analogous binuclear μ -benzoate and μ -trifluoroacetate (Pd-Pd) compounds are accessible by the same route (26).

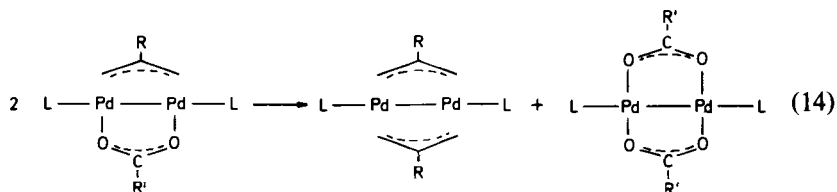


(58 - 64)

- (58) $\text{R} = \text{H}$, $\text{R}' = \text{Me}$
- (59) $\text{R} = \text{Me}$, $\text{R}' = \text{Me}$
- (60) $\text{R} = i\text{-Pr}$, $\text{R}' = \text{Me}$
- (61) $\text{R} = t\text{-Bu}$, $\text{R}' = \text{Me}$
- (62) $\text{R} = i\text{-Pr}$, $\text{R}' = \text{Ph}$
- (63) $\text{R} = t\text{-Bu}$, $\text{R}' = \text{Ph}$
- (64) $\text{R} = t\text{-Bu}$, $\text{R}' = \text{CF}_3$

The products of Eq. (13) are only partially stable in solution but do not react by disproportionation to give the symmetrical binuclear complexes $(2\text{-RC}_3\text{H}_4)_2\text{Pd}_2\text{L}_2$ and $(\text{R'COO})_2\text{Pd}_2\text{L}_2$. Instead, the mononuclear compounds $(2\text{-RC}_3\text{H}_4)\text{Pd}(\text{L})\text{OCOR}'$ are formed (26). The ligand transfer according to Eq. (14) may occur under more rigorous conditions since in the

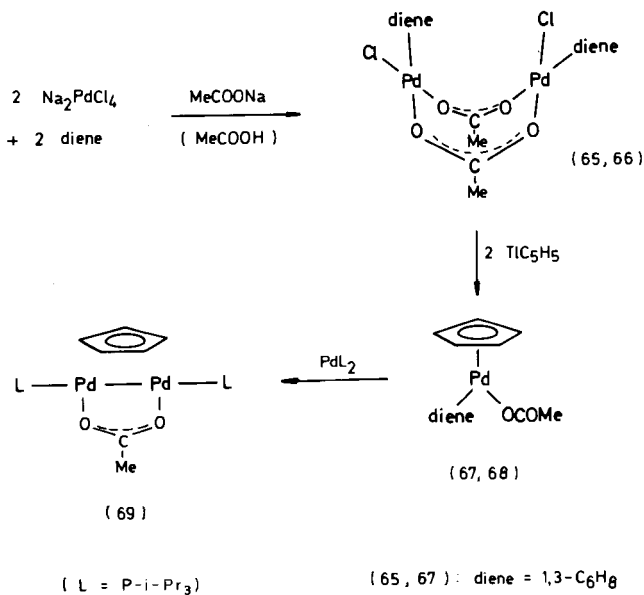
mass spectrum, e.g., of **58**, the ions $(C_3H_5)_2Pd_2L_2^+$ and $(MeCOO)_2Pd_2L_2^+$ ($L = P\text{-}i\text{-}Pr_3$) are observed.



The synthesis of $(C_5H_5)(MeCOO)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**69**), the analog of $(C_5H_5)(2\text{-}MeC_3H_4)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**12**), is shown in Scheme 4.

The intermediate diene complexes **67** and **68** containing dihapto-bonded (monodentate) diolefinic ligands are fairly labile, and are therefore preferred sources of the fragment $C_5H_5Pd(OCOMe)$ which forms the stable binuclear product **69** on treatment with $Pd(P\text{-}i\text{-}Pr_3)_2$ (**26**). The final step in the synthesis of **69** may thus be seen as a modification of the [1 + 1]-addition route.

The reaction of **69** with CF_3COOH leads to replacement of the acetate, i.e., the anion of the weaker acid, but the product is not

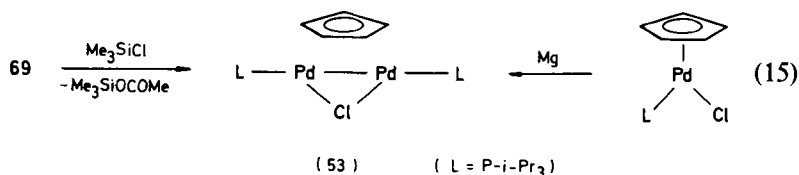


(65 , 67) : diene = 1,3-C₆H₈

(66 , 68) : diene = 1,3-C₇H₁₀

SCHEME 4

$(C_5H_5)(CF_3COO)Pd_2(P\text{-}i\text{-}Pr_3)_2$. The latter complex can be prepared by another route as shown below. Complete replacement of the acetate bridge also occurs in the reaction of **69** with Me_3SiCl , which gives $(C_5H_5)(Cl)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**53**) according to Eq. (15) (26). Felkin and Turner (27) have recently shown that this complex (already mentioned as an intermediate in the reaction sequence described in Scheme 2) can also be obtained, but in lower yields, by treatment of $C_5H_5Pd(P\text{-}i\text{-}Pr_3)Cl$ with Mg or $LiAlH(O\text{-}t\text{-}Bu)_3$. The same method allows the preparation of binuclear compounds of composition $(C_5H_5)(X)Pd_2L_2$, where X is Br and L is PPh_3 , $P\text{-}i\text{-}Pr_3$, PCy_3 , or X is I and L is $P\text{-}i\text{-}Pr_3$ (27, 28).

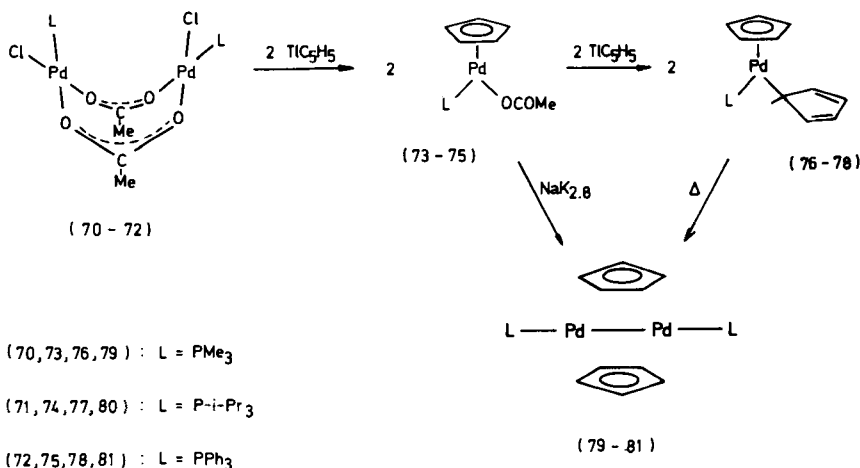


V

THE REAL SANDWICHES $(C_5H_5)_2Pd_2L_2$

After succeeding with the preparation of binuclear metal–metal bonded complexes of the types $(\mu\text{-all})(X)M_2L_2$, $(\mu\text{-}C_5H_5)(X)M_2L_2$ (X = halide or μ -carboxylate), $(\mu\text{-all})_2M_2L_2$ and $(\mu\text{-}C_5H_5)(\mu\text{-all})M_2L_2$, where M is in most cases palladium, the challenge of the synthesis of the real “sandwiches” $(\mu\text{-}C_5H_5)_2M_2L_2$ remained. We could not use the method of [1 + 1]-addition, i.e., the reaction of $(X)M(Y)$ with ML_2 , or the route of nucleophilic attack on $(X)M(Y)$ by the ligand L since the necessary starting materials $M(C_5H_5)_2$ for M = Pd and Pt are unknown (29). We therefore had to find new pathways, which for M = Pd are outlined in Scheme 5.

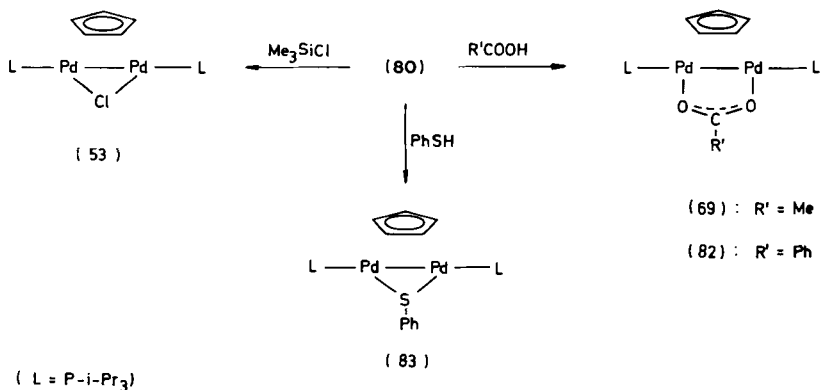
The acetate-bridged complexes **70–72** react with TlC_5H_5 in the molar ratio 1 : 2 to give the mononuclear palladium(II) compounds **73–75**, which on treatment with sodium–potassium alloy $NaK_{2.8}$ form the sandwiches **79–81** in fairly good yield (30). Reaction of **73–75** with an excess of TlC_5H_5 (molar ratio $\approx 1 : 4.4$) leads directly to the binuclear complexes without using a stronger reducing agent. This “one-pot synthesis” proceeds via **76–78** as intermediates which react probably by homolytic fission of the $Pd\text{—}\sigma\text{-}C_5H_5$ bond to yield the products. The novel dicyclopentadienyl(phosphine)palladium complexes **76–78** which are stable at low temperatures are fluxional in solution and show two independent dynamic processes (31). The process with the higher activation energy (for



SCHEME 5

which the coalescence temperature depends upon the size of the phosphine and decreases along the series $\text{L} = \text{P-}i\text{-Pr}_3 > \text{PPh}_3 > \text{PMe}_3$ is a π/σ -exchange of the two differently bound C_5H_5 ligands. The process with the lower activation energy, which for the three phosphines can be frozen out only below -80°C , is a metallotropic rearrangement, i.e., a migration of the group $(\pi\text{-C}_5\text{H}_5)\text{Pd}(\text{L})$ around the σ -bonded ring (31).

A third possible route to the binuclear sandwich complex **80** is the reaction of $(\text{C}_5\text{H}_5)(\text{MeCOO})\text{Pd}_2(\text{P-}i\text{-Pr}_3)_2$ (**69**) with TiC_5H_5 . The reverse of this particular bridge-ligand exchange also proceeds quite readily, as do the reactions of **80** with PhCOOH , PhSH , or Me_3SiCl (see Scheme 6) (30). Complex **83** is also accessible by a metathetical reaction of $(\text{C}_5\text{H}_5)(\text{Br})\text{Pd}_2(\text{P-}i\text{-Pr}_3)_2$ with TiSPh (27).



SCHEME 6

VI

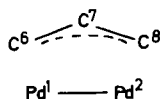
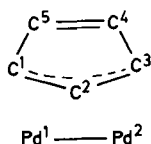
STRUCTURE AND BONDING

It has already been mentioned that probably all the complexes of general composition $(X)(Y)M_2L_2$, where $X = Y = C_5H_5$, $X = Y = \text{all}$, and $X = C_5H_5$, $Y = \text{all}$, have a sandwich-type structure, and where $X = C_5H_5$ or all and $Y = \text{halide or carboxylate}$, a half-sandwich type structure. This general statement is primarily supported by the results of several X-ray structural studies, for example on $(C_5H_5)(2\text{-MeC}_3H_4)Pd_2(PPh_3)_2$ (**8**) (5, 10), $(C_5H_5)(2\text{-MeC}_3H_4)Pd_2[P(OC_6H_4\text{-}o\text{-Me})_3]_2$ (**21**) (10), $(C_5H_5)_2Pd_2(PPh_3)_2$ (**57**) (25), $(C_5H_5)(Br)Pd_2(P\text{-}i\text{-Pr}_3)_2$ (**84**) (28), and $(C_5H_5)(I)Pd_2(PPh_3)_2$ (**56**) (22). From these results, the following conclusions can be drawn:

1. In all compounds, with the exception of the bis(allyl) complex **57**, an almost linear arrangement $P-Pd-P$ is found. In **57**, the angle $Pd-Pd-P$ deviates significantly from 180° , being 127.4° (25).

2. The $Pd-Pd$ bond length lies between 2.61 Å (for **84**) and 2.72 Å (for **57**), varying surprisingly little for the different types of bridging ligands. This relatively short distance, comparable with the interatomic distance in metallic palladium (2.74 Å), points to the existence of a direct metal–metal bond.

3. Although the C_5H_5 groups in **8** and **21** are disordered, the average distances between the palladium atoms and the ring carbon atoms in these complexes, as well as in **84**, suggest that the cyclopentadienyl ligand may not be pentahapto- but trihapto-bonded. The distances between the metal atoms and the carbon atoms of the pseudo-allyl C_5H_5 moiety, e.g., $Pd1-C1$ and $Pd2-C3$, fall within the range found for $Pd-C$ distances in simple π -allylpalladium complexes. Most importantly, the rings in **8**, **21**, and **84** are perfectly planar, not showing the type of folding found in $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)W(CO)_2$ (32).



4. The distances $Pd1-C6$ and $Pd2-C8$ in the μ -allyl complexes **8**, **21**, **56**, **57** lie between 2.10 and 2.20 Å and, therefore, do not differ from those between the palladium atoms $Pd1$ and $Pd2$ and the carbon atoms $C1$ and $C3$ of the C_5H_5 ring.

5. In the sandwich-type complexes **8**, **21**, and **57**, the two π -bonded lig-

ands are mutually parallel to each other. In the half-sandwich type complexes **56** and **84**, the planes of the allyl group and of the cyclopentadienyl group are somewhat inclined to the plane containing the halogen and palladium atoms in such a direction that the central carbon atom C2 or C7 comes closer to the metals.

The trihapto coordination of the cyclopentadienyl ring in **8**, **21**, and **84** may be present not only in the crystalline state but also in solution. This is supported by the value of the C—H coupling constant which is between the values of monohapto ($\eta^1\text{-C}_5\text{H}_5\text{—M}$) and pentahapto ($\eta^5\text{-C}_5\text{H}_5\text{—M}$) coordination. There is no doubt, however, that the binuclear ($\mu\text{-C}_5\text{H}_5$)Pd₂ complexes are fluxional in solution. The NMR spectra show [for **8** and **21** even at -60°C (10)] that the CH units of the C₅H₅ group are equivalent. The most reasonable explanation is that a very fast rotation of the five-membered ring about the axis passing through its center and oriented perpendicular to the Pd—Pd bond takes place. The axis probably does not pass through the Pd—Pd bond, so that during the rotation the C₅H₅ ligand retains its η^3 -bonding mode. The activation barrier for the rotational process is certainly very low, as found in ferrocene or other π -cyclopentadienylmetal complexes.

The electronic structure of the binuclear complexes (X)(Y)M₂L₂ (M = Pd, Pt), including the problem of "hapticity" of the bridging cyclopentadienyl ligand for X = C₅H₅, has been investigated recently on the basis of MO calculations (33). First, the fragment molecular orbitals of an M₂L₂²⁺ moiety (L = PH₃) are calculated. Their interaction with the orbitals of ligands Y[−] such as Cl[−], SR[−], RCOO[−], or C₃H₅[−] yields the wavefunctions of ($\mu\text{-Y}$)M₂L₂⁺ units and allows analysis of their bonding capability toward a second bridging group such as C₅H₅[−] or X[−] in general. As is shown schematically in Fig. 1, in the simplified MO diagram such a ($\mu\text{-Y}$)M₂L₂⁺ unit possesses only two acceptor orbitals (a₁ and b₂) which can overlap with the donor orbitals of the second bridging ligand X[−], e.g., with the 1 π and 2 π_a orbitals of C₅H₅[−]. The cyclopentadienyl ligand therefore behaves formally as a 4-electron, and not a 6-electron, donor, completely analogous to a π -bonded allyl group.

By optimizing the orientation of the (Y)M₂L₂⁺ unit below the plane of the C₅H₅ ring, the calculations also show that the barrier for a "haptotropic shift" (34) according to the process



is extremely low (33). The actual minimum of the relative position of the

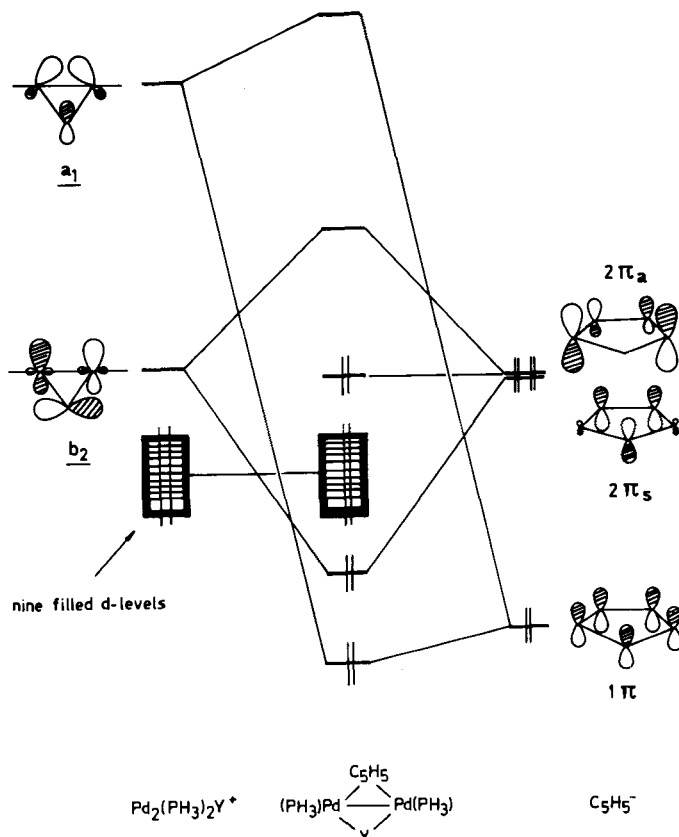


FIG. 1. Simplified MO diagram for complexes $(\mu\text{-C}_5\text{H}_5)(\mu\text{-Y})\text{M}_2\text{L}_2$ (e.g., $\text{M} = \text{Pd}$, $\text{L} = \text{PH}_3$).

cyclopentadienyl ligand strongly depends on steric interactions, and should be shifted somewhat away from the midpoint of the ring toward the C2 atom. The energy surface is definitely very "soft" and allows smooth motions of the π -bonded ligand.

The difference in C—C bond lengths in the cyclopentadienyl ring, particularly in **84**, is also in full accord with theoretical studies (33). As is seen in the diagram (Fig. 1), the $2\pi_s$ orbital of C_5H_5^- remains occupied in the binuclear complex which, due to the nodal properties of the π -molecular orbitals, leads to different bonding distances in the ring. The decrease in electron density of the $2\pi_a$ orbital strengthens the C4—C5 and weakens the C1—C5 and C3—C4 bonds, i.e., both effects favor the formation of a " π -allyl-plus-olefin" C_5H_5 system.

One further and most interesting result emerging from the MO calculations is the close relationship between the valence orbitals and bonding capacities of the M^{2+} ions and the aforementioned $M_2L_2^{2+}$ units ($M = Pd, Pt$). From this, it is not surprising that complexes $C_5H_5M(all)$ and $M(all)_2$ exist as well as those of composition $(C_5H_5)(all)M_2L_2$ and $(all)_2M_2L_2$. The molecules $(all)MX$ ($X = Cl, Br, I$) and $(all)M(OCOR')$ which are stable as dimers also have their counterparts in the species $(all)(X)M_2L_2$ and $(all)(R'COO)M_2L_2$. For Pd there are no known mononuclear complexes $M(C_5H_5)_2$, C_5H_5MX , and $C_5H_5M(OCOR')$, whereas the corresponding binuclear compounds $(C_5H_5)_2M_2L_2$, $(C_5H_5)(X)M_2L_2$, and $(C_5H_5)(R'COO)M_2L_2$ do exist. The challenge therefore remains to prepare the missing links in the mononuclear C_5H_5M series and investigate their electronic structure, particularly with regard to the hapticity problem.

VII

REACTION MECHANISM

Scheme 1 shows that formation of the binuclear complexes $(C_5H_5)(2-RC_3H_4)Pd_2L_2$, following the original synthetic pathway, should proceed via at least two intermediates. It has been assumed that one of these intermediates is the electron-deficient species PdL_2 , which can be isolated when L is a bulky phosphine, e.g., *P-i-Pr*₃ or *PCy*₃. The alternative route demonstrates that the complexes $Pd(P-i-Pr_3)_2$ and $Pd(PCy_3)_2$ can indeed serve as starting materials to form the binuclear complexes.

The question remained, however, whether the mechanistic scheme used to explain the original preparative results applied also to other ligands L, e.g., tertiary phosphites. To confirm this, kinetic studies based on NMR measurements were undertaken, particularly for the system $C_5H_5Pd(2-MeC_3H_4)/P(OMe)_3$ (20). By using *d*₈-toluene as the solvent, the ¹H-NMR signals of the cyclopentadienyl protons of the starting complex $C_5H_5Pd(2-MeC_3H_4)$ (2), the product $(C_5H_5)(2-MeC_3H_4)Pd_2[P(OMe)_3]_2$ (18), and the postulated intermediates $C_5H_5Pd(2-MeC_3H_4)P(OMe)_3$ (I₁) and $C_5H_5Pd(2-MeC_3H_4)[P(OMe)_3]_2$ (I₂) are well separated from each other, thus allowing the exact determination of the changes in concentrations. The necessary condition is that the ring protons of each of the four compounds give rise to a sharp signal, which means that the C_5H_5 ligand, not only in 2 and 18 but also in intermediate I₁, is pentahapto-bonded, whereas in intermediate I₂ it is most probably monohapto-bonded. The molecule in the latter case undergoes a very fast metallotropic rearrangement [or 1,2-shift (35)] as has been observed for $(\eta^5-C_5H_5)Pd(\eta^1-C_5H_5)PR_3$

complexes (31). There is also good evidence from NMR data that the allyl ligand in both intermediates I_1 and I_2 is monohapto-bonded and that the palladium atom in I_2 is square-planar coordinated with the two phosphite ligands in the cis position (20).

Based on the aforementioned spectroscopic studies, the following reaction sequence (1–4) for the formation of **18** can be proposed ($L = P(OMe)_3$):

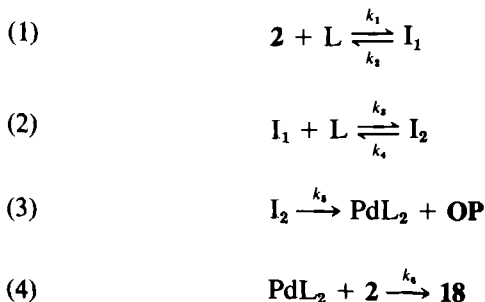


Figure 2 shows a typical diagram in which the change in concentration

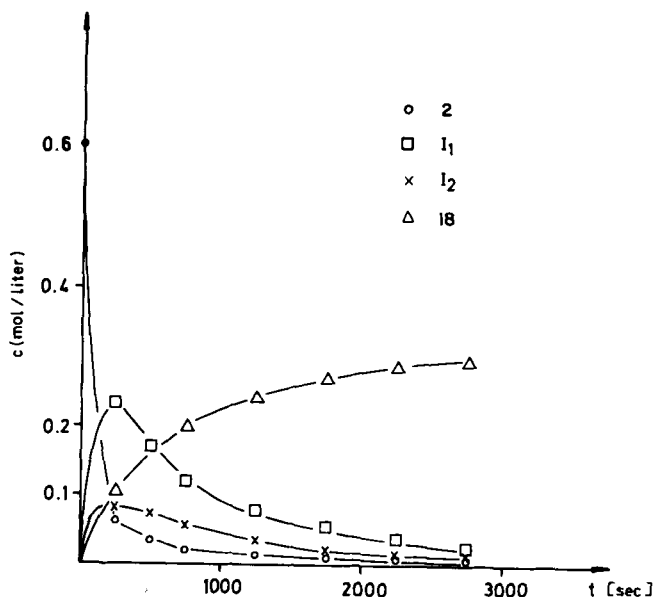


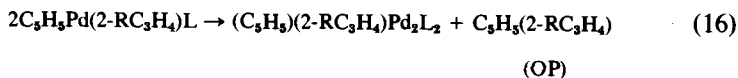
FIG. 2. Change in concentration of the starting material $C_3H_5Pd(2-MeC_3H_4)$ (**2**), the intermediates $C_3H_5Pd(2-MeC_3H_4)P(OMe)_3$ (I_1) and $C_3H_5Pd(2-MeC_3H_4)[P(OMe)_3]_2$ (I_2), and the product $(C_3H_5)(2-MeC_3H_4)Pd_2[P(OMe)_3]_2$ (**18**), during the reaction of **2** with $P(OMe)_3$ to form **18**.

of **2**, **I**₁, **I**₂, and **18** is plotted versus time. First, it is evident from these data that quantitative formation of one molecule of **18** from two molecules of **2** occurs. Second, in the beginning phase of the reaction, an appreciable amount of both intermediates **I**₁ and **I**₂ is present in the reaction mixture. The fact that the concentration of each of the intermediates goes through a maximum before decreasing to zero means that the difference in rate of the individual steps is not very large. It follows that a simple rate law cannot be expected.

Since it is not possible to solve the differential equations exactly for the six different reaction steps, the concentration curves of **2**, **I**₁, **I**₂, and **18** shown in Fig. 2 have been simulated by assuming varying numerical values for the rate constants k_1 – k_6 (20). The FORTRAN RMCHSS program proved to be excellent for this purpose. A good fit has been obtained by assuming that (i) the formation of **I**₁ (from **2** and **L**) and **I**₂ (from **I**₁ and **L**) is reversible; (ii) the slowest, and therefore rate-determining, step is the reaction of **I**₂ to give **PdL**₂ and the organic product **OP**; and (iii) the final, very fast step is the formation of the binuclear product (i.e., the [1 + 1]-addition). This means that the intermediate **PdL**₂ is formed in very low concentrations and reacts almost instantaneously with **2** to give **18**.

The results of similar calculations not using equimolar amounts of **2** and **L**, but an excess of the ligand **L**, point to (i) an increase in concentration of intermediate **I**₂ during the reaction, (ii) to the formation of **18** as an intermediate (which furthermore reacts with **L** to yield **PdL**₃ and **PdL**₄), and (iii) to the presence of rather high concentrations of **PdL**₂ of which only a small amount has a chance to attack **2** and to form **18**. Most of the intermediate **PdL**₂ reacts with **L** to produce the stable tetrakis(trimethylphosphite) complex **PdL**₄. The calculations leave no doubt that the reaction of **PdL**₂ with **C**₅**H**₅**Pd**(2-**MeC**₃**H**₄) is faster than the reaction of **PdL**₂ with **L**, a result which at first seems surprising, but which is in accord with the experimental observations. These findings also support the aforementioned assumption that the coordinatively unsaturated 14-electron complex **PdL**₂ behaves preferentially as a nucleophilic and not as an electrophilic reagent.

The successful synthesis of compounds of the general composition **C**₅**H**₅**Pd**(2-**RC**₃**H**₄)**L** (**13**) presented an opportunity to prove unambiguously that the mechanistic scheme described by reactions (1–4) is correct. Most of the mononuclear compounds **C**₅**H**₅**Pd**(2-**RC**₃**H**₄)**L** react quite smoothly at room temperature in benzene or toluene as solvent to give the binuclear complexes (**C**₅**H**₅)(2-**RC**₃**H**₄)**Pd**₂**L**₂.



The kinetic studies were performed with $C_5H_5Pd(2-MeC_3H_4)P-i-Pr_3$ (**85**) as starting material because it forms $(C_5H_5)(2-MeC_3H_4)Pd_2(P-i-Pr_3)_2$ (**12**) quantitatively at 25–45°C, and because there is no overlap of the C_5H_5 NMR signals of other compounds present in the reaction mixture. Therefore the concentrations of **85**, **12**, $C_5H_5Pd(2-MeC_3H_4)$ (**2**), and the organic product **OP** can be accurately determined.

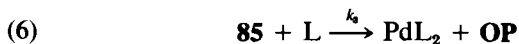
The following results have been obtained:

1. The concentrations of both **12** and **OP** increase at the same rate and in the constant ratio of 1:1. This indicates that both compounds are formed either simultaneously or, less probably, in two consecutive steps which are much faster than the first steps of the reaction.

2. The complex $C_5H_5Pd(2-MeC_3H_4)$ (**2**) is formed during the reaction, irrespective of the conditions used. The concentration is always less than 5% of the initial concentration of the starting compound **85**.

3. The rate of disappearance of **85** does not follow a constant rate law over the whole range of the reaction. Independent studies based on UV measurements (36) support the assumption that at the beginning, the decrease in concentration of **85** follows first-order kinetics, whereas near the end of the reaction, a second-order rate dependence is observed.

The most reasonable explanation is that the formation of the product **12** occurs in three steps (5–7):



By assuming steady-state conditions for intermediates **2** and PdL_2 , the rate of disappearance of **85** is given by Eq. (17).

$$-\frac{d[85]}{dt} = \frac{2k_1k_3[85]^2}{k_2[2] + k_4[85]} \quad (17)$$

In the first stage, i.e., when the concentration of the starting complex **85** is rather high and thus $k_3[85] > k_2[2]$, Eq. (17) simplifies to a first-order expression in accord with the experimental results. During the course of the reaction, the concentration of **2** reaches that of **85**, indicating that $k_2[2]$ may become equal to or even larger than $k_3[85]$ and that the rate of disappearance of **85** consequently follows a second-order rate law. The results of kinetic runs performed with addition of free $C_5H_5Pd(2-MeC_3H_4)$ (**2**) to the reaction mixture are in agreement with Eq. (17) (36).

Reaction (6) in the aforementioned sequence (5–7) corresponds to the sum of the two steps (2) and (3) proposed for the formation of $(C_5H_5)(2-MeC_3H_4)Pd_2[P(OMe)_3]_2$ (18) from **2** and $P(OMe)_3$. There is no spectroscopic evidence for the presence of an intermediate $C_5H_5Pd(2-MeC_3H_4)(P-i-Pr_3)_2$ during the reaction of **85** to give **12**. This is in accord with the previous observation (Scheme 1) that the stability of the compounds $C_5H_5Pd(2-RC_3H_4)L$ and $C_5H_5Pd(2-RC_3H_4)L_2$ strongly depends on the type of Lewis base L. When L is $P-i-Pr_3$ it becomes obvious from a molecular model that steric strain hinders formation of a stable molecule possessing two triisopropylphosphines, one σ -bonded cyclopentadienyl ring and one 2-methylallyl group as ligands.

The results of the two series of kinetic studies are in good agreement, and lead to a consistent mechanism that covers the various synthetic routes to obtain the binuclear complexes $(C_5H_5)(2-RC_3H_4)Pd_2L_2$. The overall consistency seems to be noteworthy insofar as the type of ligand L influences not only the stability of the intermediates but also the structure of compounds $C_5H_5Pd(2-RC_3H_4)L$ (13, 14). With regard to the similarities found for the different starting materials $(X)M(Y)$ the assumption can also be made that the synthesis of complexes $(C_5H_5)(all)Pt_2L_2$ (11), $(all)_2Pd_2L_2$ (25) and $(all)(X)Pd_2L_2$ (22), some of which are accessible starting from $C_5H_5Pt(all)$, $Pd(all)_2$, or $[(all)PdX]_2$ and L, may proceed by an analogous mechanistic scheme.

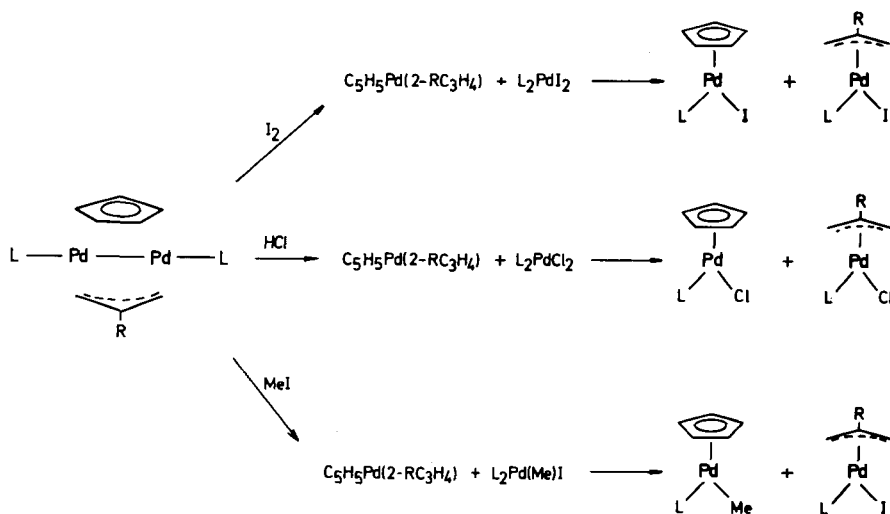
VIII

REACTIVITY

The reactions of the binuclear complexes $(X)(Y)M_2L_2$ with both electrophilic and nucleophilic reagents can be divided into two categories: those in which the binuclear skeleton is retained and those in which two mononuclear products are formed.

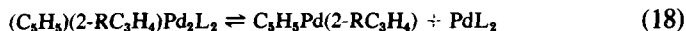
Due to their availability, most studies have been performed with compounds $(C_5H_5)(2-RC_3H_4)Pd_2L_2$ as starting materials. They react quite readily with electrophiles such as HCl, MeI, or I_2 with cleavage of the Pd—Pd bond according to Scheme 7 (11).

During the reactions, complexes $C_5H_5Pd(2-RC_3H_4)$ are formed as intermediates; they further react with L_2PdI_2 , L_2PdCl_2 , or $L_2Pd(Me)I$ to give the products. It is still undecided whether the palladium(II) compounds L_2PdX_2 and $L_2Pd(R)X$ are formed directly from $(C_5H_5)(2-RC_3H_4)Pd_2L_2$ and the electrophile or via the 14-electron species PdL_2 which, as already mentioned, quite easily undergoes oxidative addition reactions (16, 17). Evidence for a primary dissociation process according to Eq. (18) has



SCHEME 7

been obtained particularly for $\text{R} = t\text{-Bu}$ (11), but such a reaction may also occur for other less crowded dipalladium complexes.



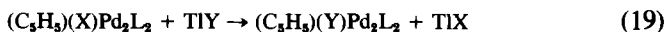
Proof for the final steps shown in Scheme 7 has been obtained by independent synthesis of both products starting from $\text{C}_5\text{H}_5\text{Pd}(2\text{-RC}_3\text{H}_4)$ and L_2PdX_2 . It should be pointed out that in the reactions of $(\text{C}_5\text{H}_5)(2\text{-RC}_3\text{H}_4)\text{Pd}_2\text{L}_2$ [$\text{R} = \text{Me}, t\text{-Bu}$; $\text{L} = \text{PMe}_3, \text{PPh}_3, \text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Me})_3$] with methyl iodide only complexes $\text{C}_5\text{H}_5\text{Pd}(\text{L})\text{Me}$ and $(2\text{-RC}_3\text{H}_4)\text{Pd}(\text{L})\text{I}$ are formed, but not those of general composition $\text{C}_5\text{H}_5\text{Pd}(\text{L})\text{I}$ and $(2\text{-RC}_3\text{H}_4)\text{Pd}(\text{L})\text{Me}$ (11).

Surprisingly, in the reactions of $(\text{C}_5\text{H}_5)(2\text{-MeC}_3\text{H}_4)\text{Pd}_2\text{L}_2$ with HBr in benzene no intermediary formation of $\text{C}_5\text{H}_5\text{Pd}(2\text{-MeC}_3\text{H}_4)$ is observed. For $\text{L} = \text{PMe}_3$, the products are $(\text{C}_5\text{H}_5)(\text{Br})\text{Pd}_2\text{L}_2$ and $(2\text{-MeC}_3\text{H}_4)\text{Pd}(\text{L})\text{Br}$ whereas for $\text{L} = \text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-Me})_3$ the complexes $(\text{C}_5\text{H}_5)(\text{Br})\text{Pd}_2\text{L}_2$ and $(2\text{-MeC}_3\text{H}_4)(\text{Br})\text{Pd}_2\text{L}_2$ are obtained. It is also possible that in these reactions [as in those of $(\text{C}_5\text{H}_5)(2\text{-MeC}_3\text{H}_4)\text{Pd}_2\text{L}_2$ with HCl] the mononuclear compounds $\text{C}_5\text{H}_5\text{Pd}(\text{L})\text{Br}$ and $(2\text{-MeC}_3\text{H}_4)\text{Pd}(\text{L})\text{Br}$ are primarily formed, and that they react with free ligand L [see, e.g., the results of Kobayashi *et al.* (22)] to yield the binuclear complexes. In general, the exact composition of the products is determined by several factors, e.g., by the ligand L , the substituent R of the allylic group and the electrophile.

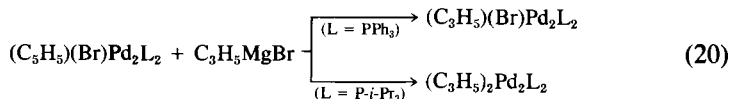
The presence of *two* bridging cyclopentadienyl ligands stabilizes the Pd_2L_2 unit. As was already shown in Scheme 6, the reactions of

$(C_5H_5)_2Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**80**) with Me_3SiCl or $R'COOH$ ($R' = CF_3, Ph$) give complexes $(C_5H_5)(Y)Pd_2(P\text{-}i\text{-}Pr_3)_2$ ($Y = Cl, R'COO$) in almost quantitative yields (**30**). Whereas **80** is inert toward MeI , it reacts with equimolar amounts of bromine to form 2 moles of $C_5H_5Pd(P\text{-}i\text{-}Pr_3)Br$ (**37**). This compound has been used as a starting material by Felkin *et al.* (**27, 28**) to prepare the binuclear complex $(C_5H_5)(Br)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**84**) following the reductive route.

The Pd_2L_2 fragment is also retained in some reactions of $(C_5H_5)(X)Pd_2L_2$ with anionic nucleophiles. A bridged-ligand exchange occurs as indicated by Eq. (19), e.g., in the reaction of $(C_5H_5)(Br)Pd_2L_2$ ($L = PPh_3, P\text{-}i\text{-}Pr_3$) with $TlSPh$ (**27**), and of $(C_5H_5)(MeCOO)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**69**) with TlC_5H_5 (**30**). In both cases, use of the thallium derivative of the reacting nucleophile Y^- seems to be of importance.



It is quite interesting that the reaction of $(C_5H_5)(Br)Pd_2(PPh_3)_2$ with C_3H_5MgBr in THF solution leads to replacement of only the C_5H_5 group, whereas the analogous complex $(C_5H_5)(Br)Pd_2(P\text{-}i\text{-}Pr_3)_2$ (**84**) reacts with the same Grignard reagent (in molar ratio 1:2) to give $(C_3H_5)_2Pd_2(P\text{-}i\text{-}Pr_3)_2$ in high yields (**27**).



The reactions of $(C_5H_5)(2\text{-}RC_3H_4)Pd_2L_2$ [and possibly also those of the analogous dipalladium complexes $(X)(Y)Pd_2L_2$] with uncharged nucleophiles, particularly with tertiary phosphines and phosphites, usually proceed by cleavage of the $Pd\text{—}Pd$ bond and coupling of the two organic groups to give the palladium(0) compounds PdL_4 .



Since the rate of formation of PdL_4 is mainly dependent on the nature and concentration of L , it may be assumed that in the primary step a nucleophilic attack of free ligand L on one of the metal atoms occurs. The mechanism would thus be similar to that of reactions of mononuclear square-planar palladium(II) complexes with Lewis bases L . In these complexes, the metal atom has a 16-electron configuration and the same is formally true for the binuclear compounds $(X)(Y)Pd_2L_2$, although the oxidation state of palladium is +1. There are nine d-electrons from the metal, two electrons from each ligand L , X , and Y , and one electron from the $Pd\text{—}Pd$ bond, thus giving the total number of 16. The simple electron counting also supports the proposition that a bridging C_5H_5 ligand be-

has like a pseudo-allyl group, donating only four instead of six electrons to the two metals.

There are some indications that the Pt_2L_2 and PdPtL_2 complexes are generally less labile than the Pd_2L_2 analogs. In the NMR spectra, e.g., of benzene solutions of $(\text{C}_5\text{H}_5)(2\text{-RC}_3\text{H}_4)\text{Pt}_2\text{L}_2$ (39, 40) and $(\text{C}_5\text{H}_5)(2\text{-RC}_3\text{H}_4)\text{PdPt}(\text{P-}i\text{-Pr}_3)_2$ (41, 42), no change is observed even after standing for several hours (20). A dynamic equilibrium according to Eq. (22) has



been confirmed for the mixed complexes $\text{PdPtCl}_4\text{L}_2$ ($\text{L} = \text{PPr}_3$, PBu_3) which possess two chloride bridges between the two different metal atoms (38).

IX

CONCLUDING REMARKS

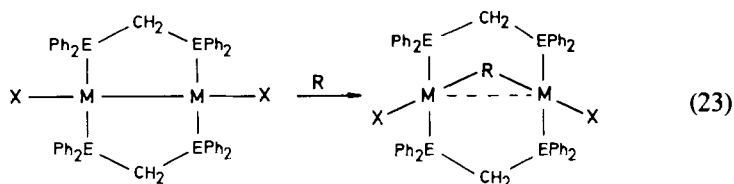
In summarizing the results obtained so far relating to the chemistry of the binuclear complexes of general composition $\text{M}_2(\mu\text{-X})(\mu\text{-Y})\text{L}_2$, two general statements can be made:

1. Most of the compounds are quite easily formed. In those cases where the corresponding mononuclear 14-electron complex ML_2 is stable, i.e., where the ligand L is a bulky phosphine such as $\text{P-}i\text{-Pr}_3$ or PCy_3 , the synthesis usually proceeds by the simple reaction of $(\text{X})\text{M}(\text{Y})$ and ML_2 . This method of [1 + 1]-addition has been applied to prepare binuclear (Pd-Pd), (Pd-Pt) and (Pt-Pt) complexes containing either one cyclopentadienyl and one allyl, two allyl, one allyl and one halide, one allyl and one carboxylate, or one cyclopentadienyl and one carboxylate group(s) as bridging ligands. Despite numerous attempts, it has not been possible to obtain the corresponding (Ni-Ni) complexes. This is probably due to the inertness of the compounds $(\text{X})\text{Ni}(\text{Y})$, in particular $\text{C}_5\text{H}_5\text{Ni}(\text{all})$ and $\text{Ni}(\text{all})_2$, as well as to the lability of the 14-electron species NiL_2 . The failure to prepare the (Ni-Ni) complexes also reflects the general trend that 4d- and 5d-elements much prefer to form metal–metal bonds than their 3d-analogs.

2. Most of the compounds are remarkably stable. Although the oxidation state of M is +1 (which is very unusual for palladium and platinum), the complexes generally react rather slowly with oxygen and tend to disproportionate to form $\text{M}(0)$ and $\text{M}(\text{II})$ compounds only in those cases where steric hindrance between the bridging groups X or Y and the terminal lig-

ands L exists. The dipalladium complexes $(C_5H_5)_2Pd_2L_2$, containing two bridging cyclopentadienyl groups, are among the most stable of the known binuclear species, a fact that is in marked contrast to the extreme lability of the mononuclear sandwich molecule $Pd(C_5H_5)_2$.

The unexpected stability of most members of the new class of compounds is certainly related to their general structure, which is characterized by two features: (a) the linear $L-M-M-L$ skeleton [the only exception being $(C_5H_5)_2Pd_2(PPh_3)_2$ (25)], and (b) for X and/or Y = all or C_5H_5 , the presence of bridging and symmetrically bonded π -allyl and π -cyclopentadienyl groups. Somewhat similar Pd(I) and Pt(I) complexes possessing a linear $X-M-M-X$ unit ($X = Cl, Br$) have been recently described by Colton (39), Brown (40), Balch (41) and their co-workers. The atoms M of these units are mainly bridged by bis(diphenylphosphino)methane or its arseno analog, so that a square-planar coordination around each metal atom results. The most interesting property of the binuclear complexes $(Ph_2ECH_2EPh_2)_2M_2X_2$ ($E = P, As$) is the capacity to react with electrophiles R (e.g., H^+ , CH_2 , $SnCl_2$, S, or SO_2), which according to Eq. (23) leads to a formal insertion of R into the metal-metal bond.



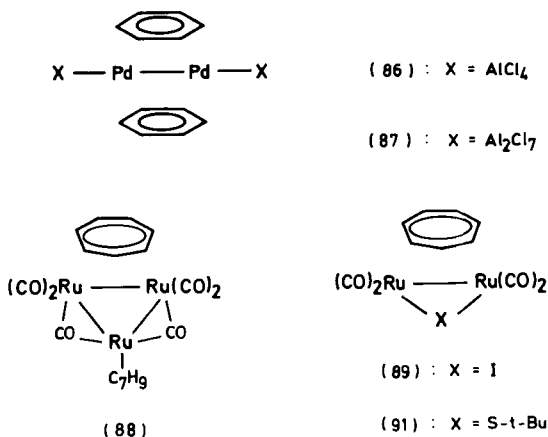
The finding that a similar electrophilic attack of R on the sandwich-type compounds $(C_5H_5)(2-RC_3H_4)Pd_2L_2$ results in the cleavage of the Pd-Pd bond can probably be explained by the different bridging groups. The frame spanned by the ditertiary phosphine or arsine ligands seems to be much tighter and allows reactions with the M_2X_2 skeleton (without destroying it) which are not possible with the M_2L_2 complexes.

The presence of simple π -allyl and π -cyclopentadienyl ligands symmetrically coordinated to an M_2 unit seems to be unique. Bridging allyl groups are found in $[C_3H_5Pt(acac)]_2$ (42) and in the tetrameric $[C_3H_5PtCl]_4$ (43), but they are linked differently to the platinum atoms, namely monohapto to one platinum and dihapto to the other. There is also no metal-metal bond formed in these complexes.

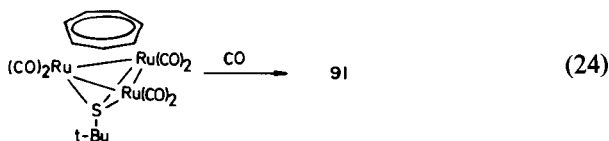
Bridging C_nH_n ring ligands coordinating a M-M fragment are known for $n = 6, 7$, or 8. That benzene is able to bridge a Pd-Pd bond was mentioned in the first paragraph of this article. Although the two complexes

(C_6H_6) $_2\text{Pd}_2(\text{AlCl}_4)_2$ (**86**) and (C_6H_6) $_2\text{Pd}_2(\text{Al}_2\text{Cl}_7)_2$ (**87**) reported by Allegra *et al.* (1, 2) are quite stable and formed in good yield, they have found no direct successors, not even with the Pt homolog. The close structural relationship between the C_6H_6 and the C_5H_5 dipalladium sandwiches [which both contain palladium(I)] is demonstrated by the linear ligand–metal–metal–ligand skeleton and by the fairly short Pd–Pd distance of about 2.60 Å, irrespective of the terminal ligands.

Bi- and trinuclear metal complexes containing a planar C_7H_7 or C_8H_8 ring linked to a metal–metal bond have been prepared in recent years, in particular by Stone and his group. The reaction of $\text{Ru}_3(\text{CO})_{12}$ with cycloheptatriene yields ($\mu_2\text{-C}_7\text{H}_7$) $\text{Ru}_3(\text{CO})_6(\eta^5\text{-C}_7\text{H}_9)$ (**88**) as the main product which reacts with I_2 to form ($\mu_2\text{-C}_7\text{H}_7$)(I) $\text{Ru}_2(\text{CO})_4$ (**89**) (44). In both compounds **88** and **89**, the cycloheptatrienyl ring bridges a Ru_2 unit, which is furthermore linked to a $\text{Ru}(\text{CO})_2\text{C}_7\text{H}_9$ fragment or an iodide ion. The C_7H_7 ligand is fluxional down to -100°C (44, 45) and thus shows a behavior completely analogous to that of the C_5H_5 ligand in the (Pd–Pd) complexes.



Following the same synthetic route, Humphries and Knox (46) succeeded in isolating structurally related ($\mu_2\text{-C}_7\text{H}_7$) Ru_3 and ($\mu_2\text{-}\eta^7\text{-C}_8\text{H}_9$) Ru_n complexes ($n = 2$ or 3) which also contain a bridging hydrocarbon ligand coordinated to two ruthenium atoms in a heptahapto mode. Most recently, the same group described the first example of a trinuclear ruthenium complex ($\mu_3\text{-C}_7\text{H}_7$)($\mu_3\text{-S-}i\text{-Bu}$) $\text{Ru}_3(\text{CO})_6$ (**90**) possessing a face-bonded cycloheptatrienyl ring (47). Compound **90** reacts with CO to form quantitatively ($\mu_2\text{-C}_7\text{H}_7$)($\mu_2\text{-S-}i\text{-Bu}$) $\text{Ru}_2(\text{CO})_4$ (**91**), a result indicating the versatility of the C_7H_7 ligand to change from a μ_3 - to a μ_2 -bonding type.



The elements of group VIII also seem most suitable for formation of bi- and trinuclear complexes containing octahapto-bonded μ_2 - or μ_3 - C_8H_8 units. One of the $C_8H_8Fe_x(CO)_y$ species formed in the reaction of iron carbonyls with cyclooctatetraene is the compound $C_8H_8Fe_2(CO)_5$, which Pettit *et al.* (48) showed possessed an eight-membered ring linked to an Fe—Fe bond. In the crystal, the C_8H_8 moiety is not completely planar, but in solution the molecule is highly fluxional, i.e., the ring is rotating rapidly relative to the metal–metal bond. It has been assumed (49) that the isoelectronic (Co—Co) complex $C_8H_8Co_2(CO)_4$ is structurally related to $C_8H_8Fe_2(CO)_5$ but this has not yet been established by X-ray analysis. A cyclooctatetraene ligand face-bonded to a M_3 triangle has been found in $(\mu_3-C_8H_8)(\mu_3-CPh)Co_3(CO)_6$ (50), $(\mu_3-C_8H_8)(C_2(CF_3)_2)Ni_3(CO)_3$ (51), and $(\mu_3-C_8H_8)(\mu_3-S)Ru_3(CO)_6$ (47); in these molecules the ring also shows fluxionality in solution. According to Stone *et al.* (51), the eight-membered ring of the Ni_3 complex may be regarded as a 6π -electron species $C_8H_8^{2+}$, an assumption which places the C_8H_8 ligand in line with the aromatic systems $C_5H_5^-$, C_6H_6 , and $C_7H_7^+$. A binuclear sandwich structure has also been confirmed for the compound $(C_8H_8)_2Ni_2$ (52); however the Ni—Ni distance seems too long for a direct metal–metal bond.

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Phase-Transfer Catalysis in Organometallic Chemistry

HOWARD ALPER

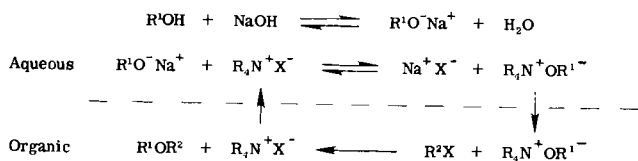
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I

INTRODUCTION

One of the major developments in organic chemistry during the past 15 years has been the application of phase-transfer catalysis to synthesis. These reactions are often effected in an aqueous base-organic two-phase system with an ammonium or phosphonium salt or crown ether as the catalyst. Crown ethers have also been of great utility as catalysts for solid-liquid phase-transfer processes. Some of the more attractive fea-



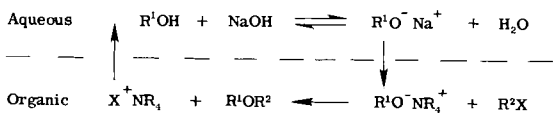
SCHEME 1

tures of phase-transfer catalytic reactions are that they can be effected under mild conditions, are rapid, and are usually simple to work up. It is a technique of considerable industrial importance.

As a basis for discussing the concept of the liquid-liquid phase-transfer process, let us consider nucleophilic substitution reactions of halides with quaternary ammonium halides functioning as catalysts. The Williamson ether synthesis, which involves displacement of halide by alkoxide, is one of the more useful substitution reactions. The alkoxide ion is generated by deprotonation of an alcohol substrate by sodium hydroxide in the aqueous phase (Scheme 1). The quaternary ammonium halide $[\text{R}_4\text{N}^+\text{X}^-]$ is then converted, by anion exchange, into a quaternary ammonium alkoxide. The latter is then transferred to the organic phase as an ion pair where it reacts with halide to give the ether and a quaternary ammonium halide, which is transported to the aqueous phase. This reaction sequence is essentially that proposed by Starks in 1971 (1). Note that the halide anion of the phase-transfer catalyst, and that of the species transferred from the organic to the aqueous phase, need not be identical (e.g., $\text{R}_4\text{N}^+\text{Cl}^-$ as catalyst, R^2Br as organic halide).

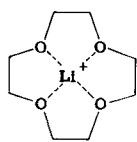
In the event that the cationic component of the phase-transfer catalyst is highly lipophilic, the scheme has to be modified in order to account for the fact that the cation will remain in the organic phase, whereas the anion can exist in both phases (Scheme 2) (2).

The principal function of crown ethers in solid-liquid phase-transfer catalysis is to bind the cation of a salt, thereby solubilizing the salt in the liquid phase and enhancing the nucleophilicity of the anion (when compared with reactions carried out in the absence of the crown ether). Of particular note among the crown ethers utilized in solid-liquid phase-transfer catalysis are 12-crown-4 to bind lithium ion (1), 15-crown-5 for

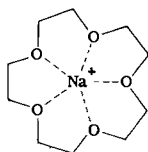


SCHEME 2

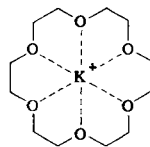
sodium ion (2), and 18-crown-6 and its relatives for tying up potassium ion (3).



(1)



(2)



(3)

Several good reviews (3–10) and books (11, 12) have been published on phase-transfer catalysis, should the reader desire a more detailed examination of the phase-transfer process. Although hundreds of examples of the application of phase-transfer catalysis to organic chemistry have appeared in the literature (13), there were, prior to 1976, no such examples in organometallic chemistry despite acceptance of the pivotal role played by organometallic anions in many stoichiometric and catalytic reactions. Since the first publication on organometallic phase-transfer catalysis (14), the field has developed sufficiently rapidly to justify an account at this time. A brief review was published by Cassar (15), and another by the same author is in press.

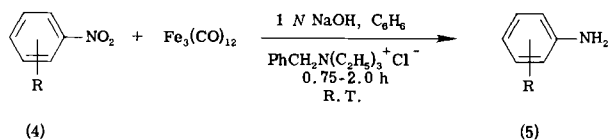
II

STOICHIOMETRIC ORGANIC REACTIONS

A. Nitro Compounds

The first experiments which were carried out in the author's laboratory on organometallic phase-transfer catalysis were concerned with the reduction of nitrobenzenes (4) to anilines (5) by triiron dodecacarbonyl. Such a conversion was reported to occur in benzene containing methanol at reflux for 10–17 h, with the hydridoundecacarbonyltriferrate anion as the likely key intermediate (16). It was our expectation that the trinuclear iron hydride should be generated by phase-transfer catalysis and if so, effect reduction of nitro compounds (4) under exceedingly mild conditions. Indeed this was the case, as illustrated by the results shown in Table I (17). Not only is the reaction complete in 2 h or less using sodium hydroxide as the aqueous phase, benzene as the organic phase, and benzyltriethylammonium chloride as the phase-transfer catalyst, but it occurs at room temperature and requires less metal carbonyl than when the reaction was

effected in a conventional manner. In fact, the reaction can be made catalytic with respect to the metal.



Crown ether catalysis of the reduction is also useful (Table I), with potassium hydroxide as the base and 18-crown-6 as the catalyst (18).

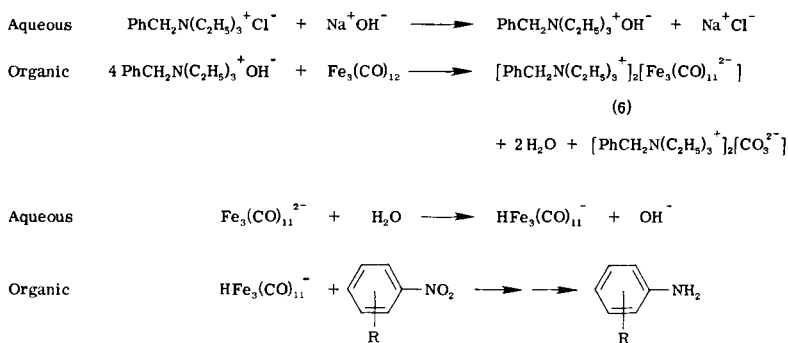
While the mechanistic details for the reduction of nitroarenes to anilines by $\text{HFe}_3(\text{CO})_{11}^-$ may prove difficult to establish (17, 19, 20), the phase-transfer-catalyzed generation of $\text{HFe}_3(\text{CO})_{11}^-$ probably proceeds via one of two pathways. In both cases, the initial step would be conversion of the quaternary ammonium halide to the corresponding hydroxide ion in the aqueous phase. The ion pair, after being transported to the organic phase, can then rapidly convert $\text{Fe}_3(\text{CO})_{12}$ (Scheme 3) to the dianion, $\text{Fe}_3(\text{CO})_{11}^{2-}$ (6), a process of some precedence (21). The dianion may then migrate to the aqueous phase to give the anionic hydride and regenerate the hydroxide ion. Attack on the nitro substrate by the iron hydride will occur after the latter has entered the organic phase.

It is also conceivable that, instead of the formation of $\text{Fe}_3(\text{CO})_{11}^{2-}$ by reaction of $\text{Fe}_3(\text{CO})_{12}$ with the quaternary ammonium hydroxide, attack by the latter at a carbonyl carbon of $\text{Fe}_3(\text{CO})_{12}$ could occur to give the hydroxycarbonyl species 7 (Scheme 4). Subsequent loss of carbon dioxide would afford the iron hydride. The intermediacy of organometallics

TABLE I
YIELDS OF ANILINES (5) OBTAINED FROM 4 AND $\text{Fe}_3(\text{CO})_{12}$ IN THE PRESENCE OR ABSENCE OF A PHASE-TRANSFER CATALYST

R (5)	Catalyst ^a	Reaction time (h)	Yield (%)	
			With catalyst	Without catalyst
<i>p</i> -CH ₃	A	2.0	85	6
<i>p</i> -CH ₃	B	1.5	65	
<i>p</i> -Cl	A	0.75	88	4
<i>p</i> -Cl	B	2.5	79	2
<i>p</i> -OCH ₃	A	2.0	92	3
<i>p</i> -OCH ₃	B	2.0	78	3
H	B	2.5	60	

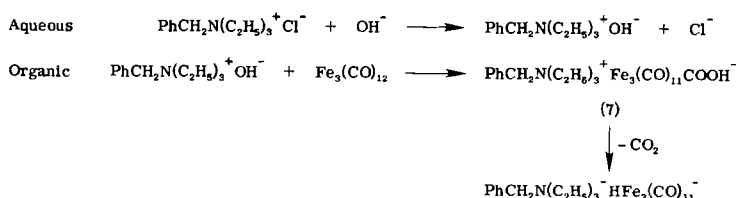
^a A = $\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3^+\text{Cl}^-$; B = 18-crown-6.



SCHEME 3

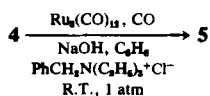
bearing hydroxycarbonyl ligands in other phase-transfer reactions will be discussed later.

When the phase-transfer process was repeated using a carbon monoxide rather than a nitrogen atmosphere for the nitro reduction, the yield of amine was significantly reduced and the organometallic complexes $(\text{RN})_2\text{Fe}_3(\text{CO})_9$ and $(\text{RN})_2\text{Fe}_2(\text{CO})_8$ were isolated as low-yield by-products. What these results imply is that carbon monoxide either retards ligand dissociation of an intermediate or adds to the dissociated species reducing the rate of any subsequent reaction (19).



SCHEME 4

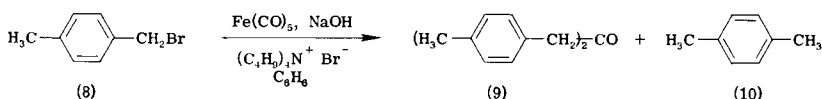
What is especially intriguing is the reverse behavior exhibited by the use of ruthenium carbonyl as the metal carbonyl. This reaction, which is catalytic in both $\text{Ru}_3(\text{CO})_2$ and quaternary ammonium halide (which accelerates the rate of formation of the hydride intermediate), occurs in much higher yield under a carbon monoxide than a nitrogen atmosphere (22). The reaction conditions used for the $\text{Ru}_3(\text{CO})_{12}$ -catalyzed reaction are much milder than those reported using the water gas shift reaction [100°C, 500 psi] (23).



The simpler iron carbonyls, $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_9$, can also deoxygenate nitrobenzenes to anilines in an aqueous base-organic solvent system. With these carbonyls, however, a phase-transfer catalyst is not only unnecessary, its presence results in reduced product yields! Furthermore, the nitro compound *must* be present to induce attack of hydroxide ion on $\text{Fe}(\text{CO})_5$ to give $\text{HFe}(\text{CO})_4^-$ [and possibly $\text{HFe}_2(\text{CO})_8^-$] (17). Such a phenomenon was also noted by Pettit and co-workers (23) in their excellent work on the use of water gas shift reaction conditions for the $\text{Fe}(\text{CO})_5$ -catalyzed deoxygenation of nitrobenzenes.

B. Halides

The reaction of halides (e.g., **8**) with iron pentacarbonyl, base, and tetrabutylammonium bromide as the catalyst has been reported to give ketones (e.g., **9**) and variable amounts of hydrocarbons (e.g., **10**). The latter was the major product formed at low base concentration while the ketone was the exclusive or predominant product at high base concentration (24). The tetracarbonylferrate(II) species, $\text{Fe}(\text{CO})_4^{2-}$, is the supposed reagent



% NaOH	Product distribution	
	(9)	(10)
2.0	33	67
3.8	50	50
16.6	85	15
33	95	5

at high concentration while $\text{HFe}(\text{CO})_4^-$ is postulated to exist at low base concentration. It should be noted that $\text{HFe}(\text{CO})_4^-$ has in fact been isolated, in small amounts, by phase-transfer-catalyzed reaction of $\text{Fe}(\text{CO})_5$ with *concentrated* sodium hydroxide (5 mmol/0.4 ml of water) (25). Whereas the phase-transfer catalyst is required for the formation of ketones, it is unclear whether it is really necessary for the production of hydrocarbons such as **10**. Furthermore, it remains to be seen whether the

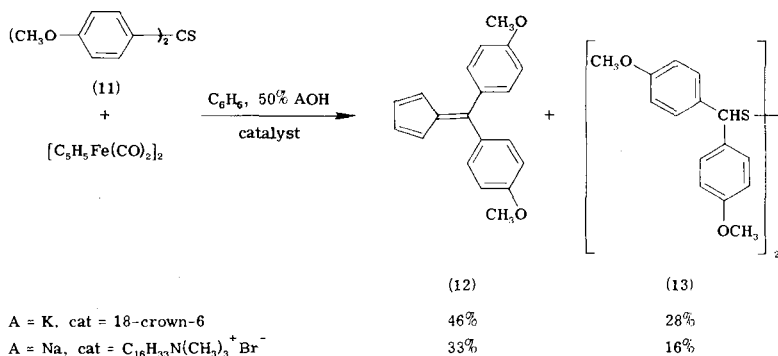
proposed, or other [e.g., $\text{HFe}_2(\text{CO})_8^-$] anions are involved in these reactions.

C. α,β -Unsaturated Ketones

The two-phase reduction of nitro compounds to anilines by $\text{Fe}_3(\text{CO})_{12}$, potassium hydroxide, and 18-crown-6 has previously been described (18). Crown ether catalysis (18-crown-6 or dicyclohexyl-18-crown-6) is also useful for reducing the double bond of the α,β -unsaturated ketone, benzylideneacetone. Either of the following reaction systems can be employed: $\text{Fe}(\text{CO})_5/\text{KOH}/\text{crown ether}/\text{benzene}$ or $\text{Fe}(\text{CO})_5/\text{RNH}_2/\text{H}_2\text{O}/\text{crown ether}/\text{benzene}$ (26).

D. Thiobenzophenones

Thiobenzophenones undergo a novel desulfurization and coupling reaction with the *in situ* generated cyclopentadienylmetal carbonyl anions [$\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_n^-$; $\text{M} = \text{Mo}, \text{W}, n = 3$; $\text{M} = \text{Fe}, n = 2$] to give fulvenes in low to moderate yields, with disulfides formed as by-products. The highest yields were realized using crown ether catalysis (e.g., **11** \rightarrow **12** and **13**). Although product yields were lower using a quaternary ammonium salt as the catalyst, they were nevertheless superior to those obtained by generation of the metal carbonyl anion by exposure of the dimer to sodium-potassium alloy in tetrahydrofuran under rigorously anhydrous conditions (27).



III

CATALYTIC ORGANIC REACTIONS

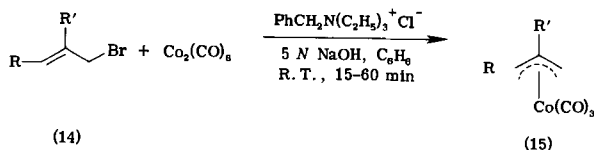
A. The Cobalt Tetracarbonyl Anion

One of the most important metal carbonyl anions, as far as catalytic processes are concerned, is the cobalt tetracarbonyl anion, $\text{Co}(\text{CO})_4^-$. Prior to attempting phase-transfer catalysis using $\text{Co}(\text{CO})_4^-$ as a catalyst, it was imperative to establish that the anion is actually formed under these conditions. Therefore, model experiments in the author's laboratory involved the initial use of dicobalt octacarbonyl in a stoichiometric role.

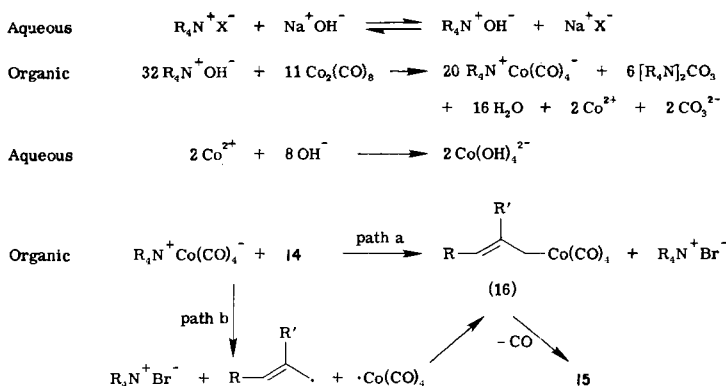
Allyl bromides (**14**) react, at room temperature, with a stoichiometric quantity of $\text{Co}_2(\text{CO})_8$, sodium hydroxide (5 *N*), benzene, and benzyltriethylammonium chloride as the phase-transfer catalyst. Fine yields (Table II) of π -allylcobalt tricarbonyl complexes (**15**) were obtained by use of short reaction times (15–60 min) (28). This simple and mild method is superior to conventional routes described in the literature (29–31).

Under a nitrogen atmosphere, cobalt carbonyl probably experiences disproportionation by base (Scheme 5) to give $\text{Co}(\text{CO})_4^-$. One of the disproportionation by-products is the $\text{Co}(\text{II})$ ion which gives a blue color in aqueous NaOH due to the presence of small amounts of the $\text{Co}(\text{OH})_4^{2-}$ ion. The subsequent reaction of the cobalt tetracarbonyl anion with **14** is probably a displacement (path a), giving the σ -allyl complex **16**. However, the possibility of an electron-transfer pathway (path b), either as an alternative to, or concurrent with, the displacement pathway cannot be dismissed at this time.

TABLE II
REACTION TIMES AND YIELDS OF **15**



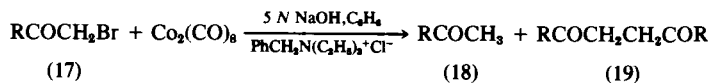
R,R' (15)	Reaction time (min)	Yield (%)
H,H	15	80
H,CH ₃	40	73
CH ₃ ,H	15	80
Ph,H	60	72



SCHEME 5

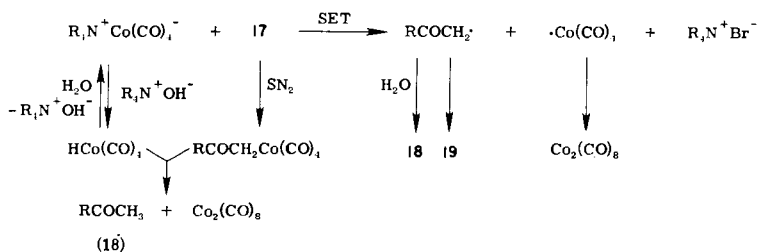
The crown ether-catalyzed generation of the $Co(CO)_4^-$ ion in ether or hydrocarbon solvents has been described (32). Treatment of the anion with 2,3-bis(bromomethyl)naphthalene in tetrahydrofuran gives what is formulated as a bis- π -allyl complex, while ketones were isolated using monocyclic dibromides as substrates.

Activated halides, such as α -bromo ketones (17), can be dehalogenated in the presence of catalytic amounts of both $Co_2(CO)_8$ and $PhCH_2N-(C_2H_5)_3^+Cl^-$. One way of accounting for the formation of monoketones (18) and in some instances, 1,4-diketones (19), is by single-electron trans-

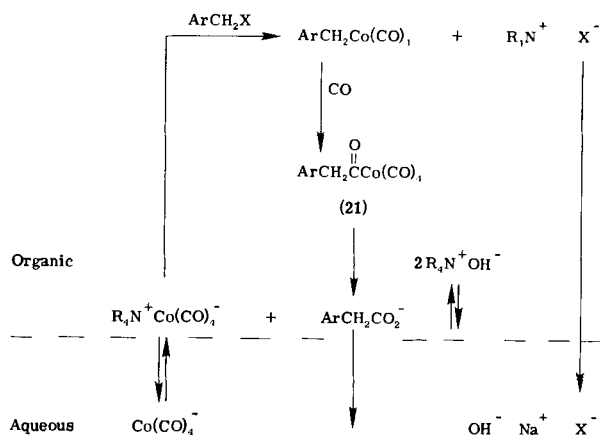


fer (Scheme 6) from the cobalt tetracarbonyl anion to the α -halo ketone (33).

Let us now again consider the phase-transfer-catalyzed conversion of $Co_2(CO)_8$ to $Co(CO)_4^-$. As noted in Scheme 5, the disproportionation

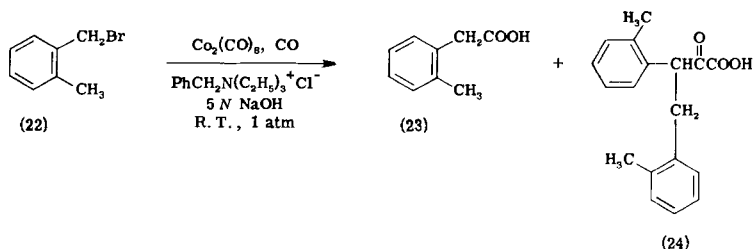


SCHEME 6



SCHEME 8

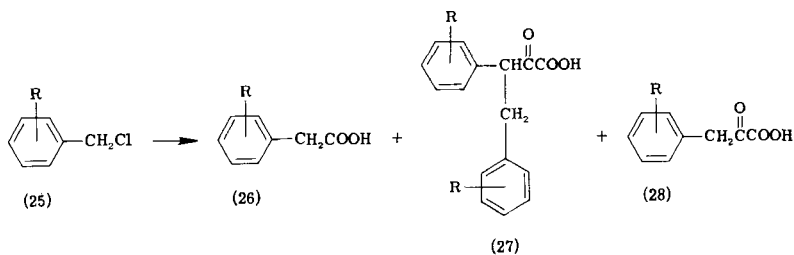
tent using *o*-, *m*-, or *p*-methylbenzyl chloride (**25**, R = *o*-, *m*-, *p*-CH₃) as substrates at 60°C. A nonalkylated double carbonylation product, **28**, and



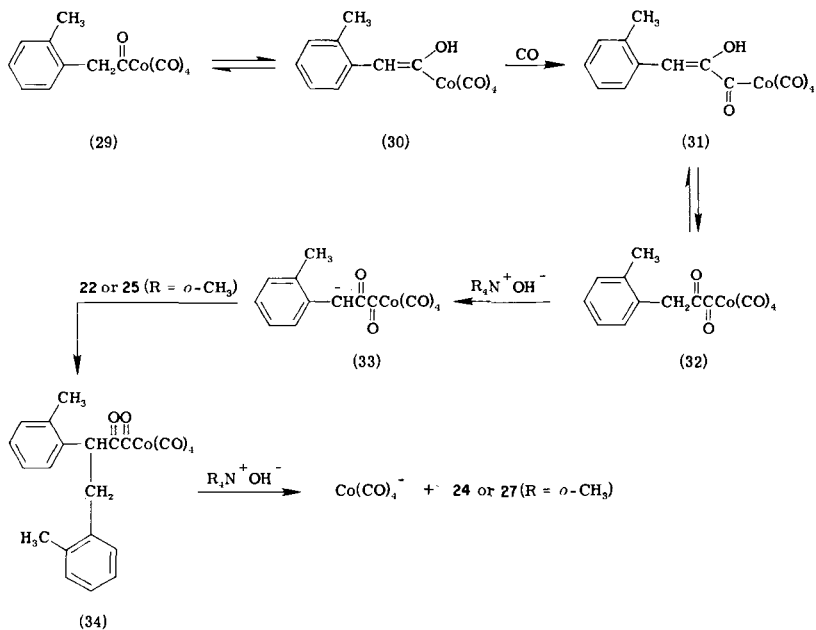
26 [R = 2,4,6-(CH₃)₃], was formed in equal proportions for **25**, R = 2,4,6-(CH₃)₃, while the unsubstituted and the *m*-trifluoromethyl-substituted benzyl chlorides (**25**, R = H, *m*-CF₃) afforded only the phenylacetic acid (**26**, R = H, *m*-CF₃) (Table III) (38).

Enolization of the intermediate acylcobalt tetracarbonyl **29** (analogous to **21**) to **30** may be the key to the double carbonylation reaction [Scheme 9, illustrated for **22** or **25** (R = *o*-CH₃) as substrates]. The conjugated vinylcobalt complex can undergo carbonyl insertion (ligand migration) giving the enol **31** which can then be in tautomeric equilibrium with the α -diketone **32**. The presence of the α -diketone function in **32** enhances the acidity of the benzylic hydrogens relative to those of **29**. Consequently, proton abstraction by base (**33**) and subsequent alkylation would give **34**. Cobalt-carbon bond cleavage of **34** by the quaternary ammonium hy-

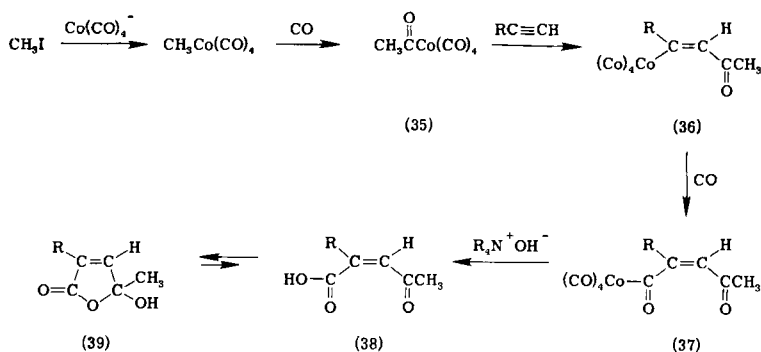
TABLE III
PRODUCT DISTRIBUTION AND YIELDS OF 26-28



25 (R)	Yield (%)	Product distribution		
		26	27	28
H	60	100	—	—
<i>m</i> -CF ₃	34	100	—	—
<i>o</i> -CH ₃	78	60	40	—
<i>m</i> -CH ₃	58	82	18	—
<i>p</i> -CH ₃	75	70	30	—
2,4,6-(CH ₃) ₃	21	50	—	50



SCHEME 9

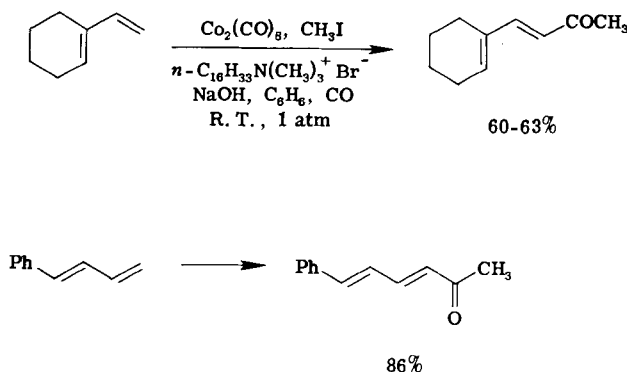


SCHEME 10

dioxide affords the alkylated phenylpyruvic acid and regenerates the cobalt tetracarbonyl anion. The nonalkylated phenylpyruvic acid **28**, $\text{R} = 2,4,6\text{-(CH}_3)_3$, may arise from cobalt-carbon bond cleavage of the 2,4,6- $(\text{CH}_3)_3$ analog of **32**, since the presence of methyl substituents at *both* ortho positions could provide steric hindrance to proton abstraction by the quaternary ammonium hydroxide.

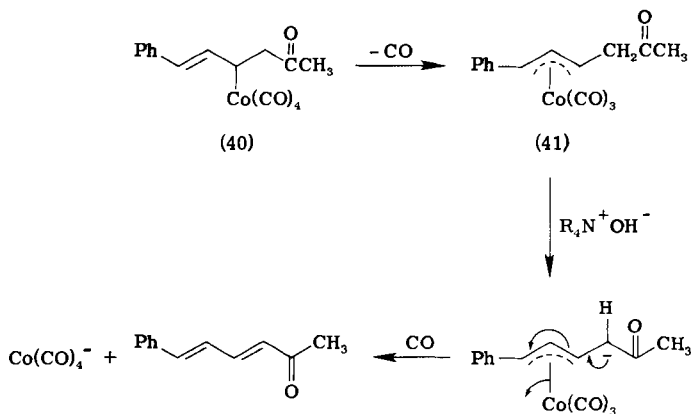
The acylcobalt tetracarbonyl intermediate of Schemes 8 and 9 can be intercepted by effecting the carbonylation of halides in the presence of alkynes, dienes, and trienes. Cobalt carbonyl can catalyze the reaction of alkynes with carbon monoxide and methyl iodide as the halide, under phase-transfer conditions, to give the pharmacologically important 2-butenolides (**39**). This regiospecific reaction may proceed by addition of the *in situ* generated acetylcobalt tetracarbonyl (**35**) to the alkyne giving a vinylcobalt complex (**36**). Carbonylation of **36**, like that of **30** (Scheme 10), would give **37**. Metal-carbon bond rupture by base would produce the unsaturated keto acid (**38**) which is the chain tautomer of the cyclic lactone **39**. This reaction pathway is different from the one effected by conventional means, where **37** rearranges to a cyclic π -allyl complex. Although the latter process is interesting, it is of no practical use from an organic chemistry viewpoint (**40**).

Use of a diene or triene, in place of an alkyne, in reaction with methyl iodide and a catalytic amount of cobalt carbonyl, gives (*E*)-conjugated enones in a highly regiospecific manner (**41**). Not only is this a much milder reaction than that reported using standard conditions [50–85°C, 50–130 psi (**42**)], but the yields of pure isolated materials are significantly higher as well. There is some, but not conclusive, evidence for 1,2-addition of acetylcobalt tetracarbonyl (**35**) to the least-substituted double bond of the diene or triene affording a σ -allyl complex [e.g., **40** (derived from



1-phenyl-1,3-butadiene) Scheme 11]. Loss of carbon monoxide from **40** would give the π -allyl complex **41** which, unlike **15**, has acidic hydrogens and can therefore be deprotonated by base to form carbanion **42**, possessing substantial sp^2 character. It is the latter property that may govern the stereochemistry of decomplexation of **42** to the thermodynamically more stable (*E*)-dienone.

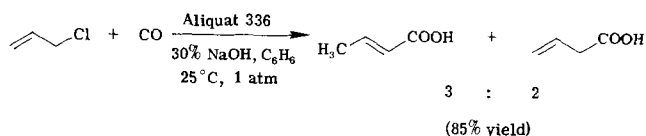
It is important to note that even certain phase-transfer *catalysts* can be carbonylated to carboxylic acids, *not* by cobalt tetracarbonyl anion catalysis, but by acetylcobalt tetracarbonyl. This is a slow but high-yield reaction that occurs for quaternary ammonium salts that are capable of forming reasonably stable free radicals. For example, phenylacetic acid is formed in 95% yield from benzyltriethylammonium chloride (benzyl radi-



SCHEME 11

cal) while carbonylation is not observed in the cases of cetyltrimethylammonium or tetrabutylammonium bromide salts, which could only generate simple primary radicals. These results, together with previous discussions relating to Schemes 5 and 6, suggest serious consideration of the possible participation of free radicals in certain organometallic phase-transfer processes. Furthermore, one obviously should *not* use benzylic, naphthylmethyl, or related ammonium halides (ephedrinium halides) as phase-transfer catalysts for sluggish cobalt-catalyzed reactions (43).

Bis(triphenylphosphine)palladium dichloride $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$ can also be used as a catalyst for the phase-transfer carbonylation of halides. However, considerably more drastic conditions $[95^\circ\text{C}, 5 \text{ atm}]$ are required when compared with $\text{Co}_2(\text{CO})_8$ (44). The carbonylation of allyl chlorides can be catalyzed by nickel tetracarbonyl, giving isomeric mixtures of butenoic acids. There is evidence for the intermediacy of polynuclear nickelates in this phase-transfer process (45). Acetylene insertion did not occur



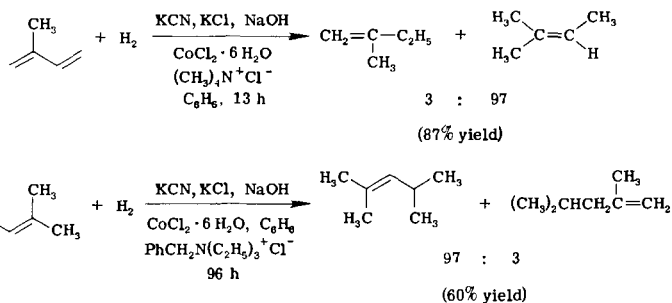
Aliquat 336 = Tricaprylmethylammonium chloride

when the carbonylation was run in the presence of the alkyne, probably because the intermediate anion lacks halogen. The latter may be essential for any subsequent alkyne insertion.

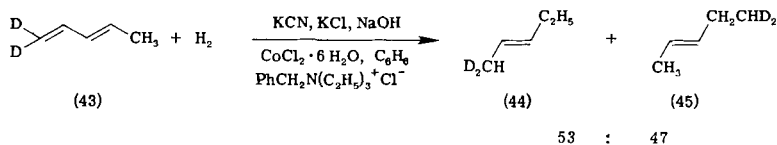
C. Hydrogenation

Water-soluble rhodium complexes bearing sulfonated triphenylphosphine ligands can catalyze the reduction of cyclohexene in a two-phase system. It is also possible to use Wilkinson's catalyst $[(\text{Ph}_3\text{P})_3\text{RhCl}]$ for the hydrogenation of water-soluble olefins in an aqueous-benzene solvent system (46).

Conjugated dienes can be reduced to monoolefins by treatment with hydrogen, hydrated cobalt chloride, potassium cyanide, potassium chloride, sodium hydroxide, and tetramethylammonium chloride or benzyltriethylammonium chloride as the phase-transfer catalyst. The hydridopentacyanocobaltate anion, $\text{HCo}(\text{CN})_5^{3-}$, is the probable metal catalyst (47-

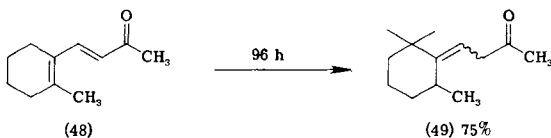
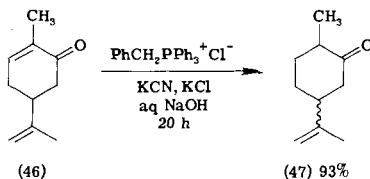


49). The functions of the phase-transfer reagent are to accelerate the rate of hydrogenation and to prevent catalyst decomposition. The reaction occurs by both 1,2- and 1,4-addition, as indicated by the formation of both



44 and 45 from 1,1-dideutero-1,3-pentadiene (47, 49). The use of micelles for the reduction of dienes has also been reported (47, 50).

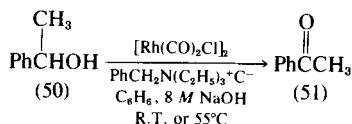
α,β -Unsaturated ketones can be hydrogenated, at the double bond, using $\text{HCo}(\text{CN})_5^{3-}$ as the hydrogenation catalyst and benzyltriphenylphosphonium chloride as the phase-transfer catalyst. This reduction is less facile than that of dienes, with substitution α to the carbonyl group increasing the rate of reaction, and β -substitution retarding or completely inhibiting hydrogenation. Examples include the reduction of car-



vone (46) to the ketone (47) in 93% yield (6:1 trans–cis mixture), and net 1,4-addition of hydrogen to β -ionone (48) affording the (*Z*)- and (*E*)-isomers of 49 in a 2:3 ratio [methyl sorbate behaves similarly (51)]. Mechanistic experiments suggest that the phase-transfer catalyst stabilizes the hydrogenation catalyst against decomposition, but that otherwise this is not a genuine phase-transfer process (49).

D. Dehydrogenation

Alcohols can be dehydrogenated to carbonyl compounds by exposure to a catalytic amount of a rhodium(I) complex under phase-transfer conditions. This reaction is particularly useful for benzylic alcohols such as 1-phenylethanol (50) which gave acetophenone (51) in 78% yield using chlorodicarbonylrhodium(I) dimer as the metal catalyst and benzyltriethylammonium chloride or Aliquat 336 as the phase-transfer catalyst (52).



The reaction will occur in the absence of the quaternary ammonium salt (i.e., as a two-phase reaction) but with reduced product yields. Primary alcohols are less reactive than secondary alcohols, and reaction of the latter can be carried out in the presence of the former [e.g., only the secondary alcohol of $\text{PhCH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$ undergoes dehydrogenation]. In these reactions, the phase-transfer catalyst may convert the alcohol to the alkoxide ion and, as well, displace the bridging chloride ligand of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ by hydroxide or alkoxide.

E. Isomerization

When allylic alcohols were used as substrates for dehydrogenation catalyzed by rhodium(I) complexes, isomerization to carbonyl compounds occurred instead. The product yields were excellent (Table IV) and the remarkably mild reaction could be effected in the absence of the phase-transfer catalyst with nearly as good results (53). Hydroxy- π -allylrhodium complexes are probable reaction intermediates.

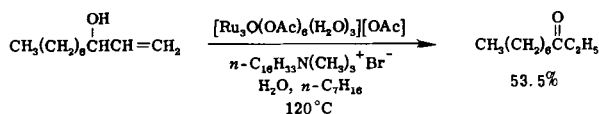
A report has described the same type of isomerization using μ_3 -oxo-triruthenium acetate as the metal catalyst and heptane as the organic

TABLE IV
 BIPHASIC RHODIUM(I)-CATALYZED ISOMERIZATION OF ALLYL ALCOHOLS

Allyl alcohol	$\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3^+\text{Cl}^-$	Product	Yield (%)
$\text{CH}_2=\text{CH}\overset{\text{OH}}{\underset{ }{\text{CH}}}\text{C}_3\text{H}_7$	Yes	$\text{C}_2\text{H}_5\text{COC}_3\text{H}_7$	100
	No	$\text{C}_4\text{H}_5\text{COC}_3\text{H}_7$	90-93
$\text{CH}_3\text{CH}=\text{CH}\overset{\text{OH}}{\underset{ }{\text{CH}}}\text{CH}_3$	Yes	$\text{CH}_3\text{COC}_3\text{H}_7$	98
	No	$\text{CH}_3\text{COC}_3\text{H}_7^a$	80
$\text{Ph}\overset{\text{OH}}{\underset{ }{\text{CH}}}\text{CH}=\text{CH}_2$	No	PhCOC_2H_5	71
$\text{PhCH}=\text{CH}\overset{\text{OH}}{\underset{ }{\text{CH}}}\text{CH}_3$	Yes	$\text{PhCH}_2\text{CH}_2\text{COCH}_3$	94

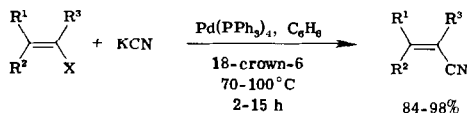
^a An unidentified by-product was also formed.

phase. Unfortunately, conversions are average and the reaction requires the use of high temperatures (54).



F. Cyanation

In 1977, Yamamura and Murahashi (55) described the palladium(0)-catalyzed cyanation of vinyl halides in the presence of a crown ether catalyst. The isolated yields of unsaturated nitriles were excellent, especially



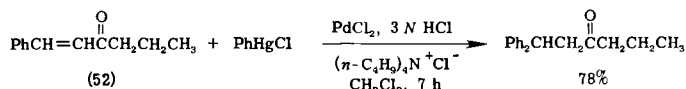
when 18-crown-6 was used as the crown ether.

The reaction was more recently applied to aromatic halides with tris(tri-phenylphosphine)nickel(0) as the metal catalyst (56). This transformation could be carried out in the same manner as for vinyl halides, or by use of

an aqueous-organic two-phase system in the presence of either a crown ether or a quaternary ammonium salt.

G. Phenylation

Phenylation of α,β -unsaturated ketones can be attained by reaction with phenylmercuric chloride or tetraphenyltin (usually 1.5 equivalents) catalyzed by an acidic solution of palladium chloride and tetrabutylammonium chloride (57). The reaction is limited to substrates containing a disubstituted double bond such as **52** (i.e., cholest-4-en-3-one and 3,5,5-trimethyl-2-cyclohexen-1-one are inert).



IV

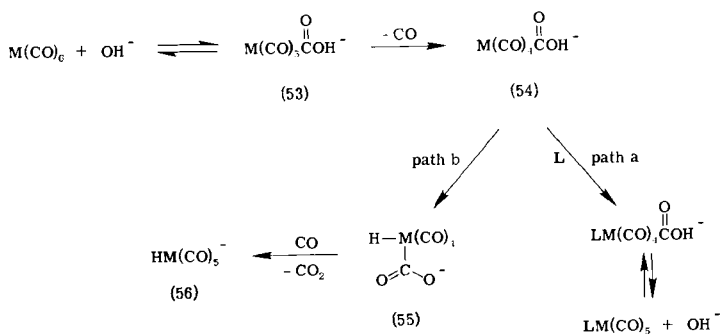
ORGANOMETALLIC SYNTHESIS

A. Ligand Substitution

Phase-transfer catalysis can effectively promote the substitution of group 6 metal carbonyls by nitrogen, phosphorus, and arsenic ligands. Reaction of $\text{M}(\text{CO})_6$ [$\text{M} = \text{Cr}, \text{Mo}, \text{W}$] with a group 5 ligand and tetra-*n*-butylammonium iodide in benzene-sodium hydroxide (50%), at 25–80°C

TABLE V
LIGAND-SUBSTITUTION PRODUCTS OBTAINED FROM EQUIMOLAR AMOUNTS
OF $\text{M}(\text{CO})_6$ AND L IN C_6H_6 /50% NaOH

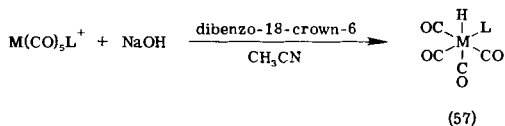
Ligand (L)	M	Temperature (°C)	Reaction time (h)	Products	Yield (%)
diphos	Cr	80	2	$[\text{Cr}(\text{CO})_4\text{L}]$	63
	Mo	80	2	$[\text{Mo}(\text{CO})_4\text{L}]$	91
	Mo	25	2	$[\text{Mo}(\text{CO})_4\text{L}]$	87
	W	80	2	$[\text{W}(\text{CO})_4\text{L}]$	75
	W	25	2	$[\text{W}(\text{CO})_4\text{L}]$	51
dipy	Mo	80	4	$[\text{Mo}(\text{CO})_4\text{L}]$	70
AsPh ₃	Mo	80	2	$[\text{Mo}(\text{CO})_5\text{L}]$	53



SCHEME 12

resulted in the formation of the ligand substitution product in 51–94% yield. Some examples are given in Table V (58). Hui and Shaw proposed that nucleophilic attack by the hydroxide ion at a carbonyl carbon of M(CO)_6 would give an anionic hydroxycarbonyl complex (53) which, followed by ligand substitution and hydroxide ion loss, would afford the product. Brown and Bellus (59) have noted the cis-labilizing properties of the hydroxycarbonyl ligand and have proposed path a of Scheme 12 as the mechanism for the ligand substitution process. The key 16-electron ligand complex (54) may also rearrange to the hydride (55) and then lose carbon dioxide to give 56 (path b). Recent experimental results of Darensbourg and co-workers (60) suggest that the phase-transfer catalysis process cannot be satisfactorily accounted for by simple CO labilization by the COOH ligand. While Mo(CO)_4 diphos was obtained in 74% yield from the reaction of Mo(CO)_6 and bis(1,2-diphenylphosphino)ethane at 29°C, $\text{Mo(CO)}_5^{13}\text{CO}$ accounted for only 10% of the Mo(CO)_6 isolated from the reaction of Mo(CO)_6 with ^{13}CO under identical conditions. Since phosphine substitution occurs much more rapidly than either ^{13}CO substitution or oxygen exchange, the incoming ligand must have a significant influence on the rate of product formation.

An investigation of the reaction of group 6 metal carbonyls with OH^- in the absence of a Lewis base ligand indicates that oxygen exchange is a much more facile process than elimination of carbon dioxide from 53 (61).

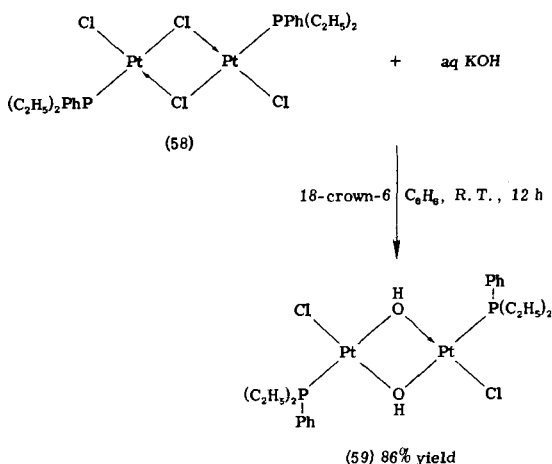


$\text{M} = \text{Mn}, \text{L} = \text{PPh}_3, \text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3, \text{P}(\text{CH}_3)_2\text{Ph}$

$\text{M} = \text{Re}, \text{L} = \text{PPh}_3$

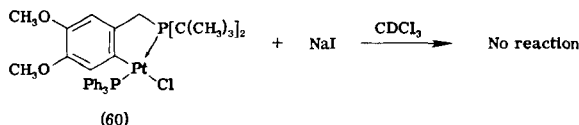
For the group 7B cations, $M(\text{CO})_5\text{L}^+$ ($M = \text{Mn, Re}$), reaction with hydroxide ion in acetonitrile containing dibenzo-18-crown-6 results in acceleration of the rate of formation of the hydroxycarbonyl intermediate, and of the subsequent elimination of carbon dioxide to give the *cis*-hydride **57** (62, 63).

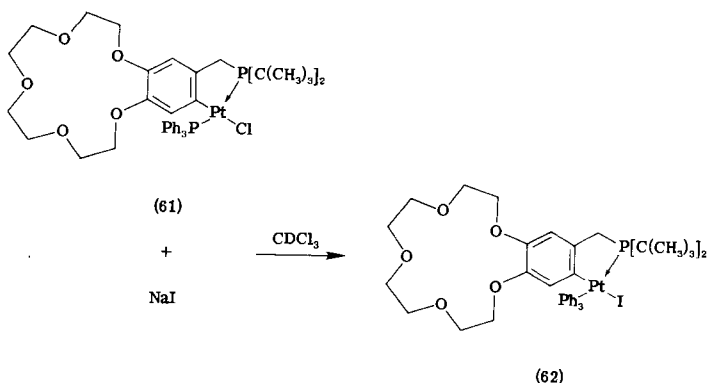
The synthesis of bridging hydroxo complexes of platinum has been reported by Fakley and Pidcock (64). Treatment of bridging chloro complexes (e.g., **58**) with aqueous potassium hydroxide, benzene, and a



crown ether catalyst affords the corresponding hydroxo complexes (e.g., **59**). Cyanide ion can similarly displace a neutral ligand [e.g., $\text{P}(\text{C}_2\text{H}_5)_3$] of mononuclear platinum complexes. Halide interchange has also been observed for some anionic osmium complexes (65) and for silacyclohexadiene compounds (66).

A good example of internal crown ether catalysis of a halide displacement reaction has been demonstrated for a phosphorus donor ligand cycloplatinated complex (67). Whereas the dimethoxy-substituted platinum chloride complex **60** does not react with sodium iodide, the benzo-15-crown-5 analog (**61**) readily undergoes ligand substitution, under identical reaction conditions, to give **62**. The crown ether moiety of **61** functions as its own phase-transfer agent.





B. σ - and π -Allyl Complexes

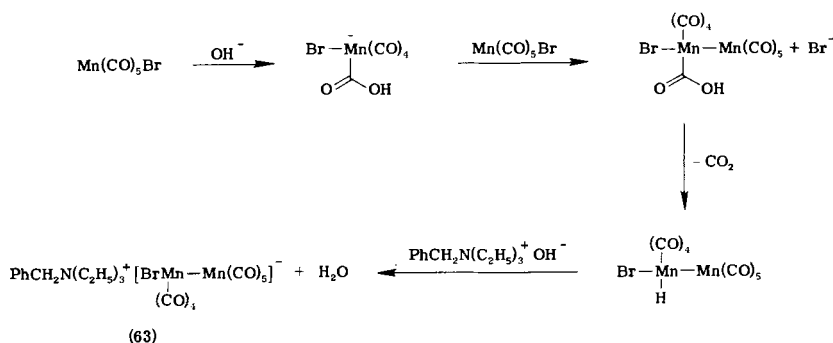
Although, as noted earlier, phase-transfer catalysis is an excellent method for the synthesis of π -allylcobalt carbonyl complexes from allyl bromides and cobalt carbonyl, the use of other metal carbonyls [e.g., $\text{Mn}_2(\text{CO})_{10}$] gave disappointing results [e.g., 20–30% yields of $(\pi\text{-allyl})\text{Mn}(\text{CO})_4$]. Gibson and co-workers (68–70) developed an elegant approach to the synthesis of π - and σ -allyl manganese, molybdenum, iron, and ruthenium complexes using metal carbonyl halides and allyl halides as reactants. π -Allyl complexes are the usual reaction products (Table VI), although σ -allyl complexes were isolated in several instances. This phase-transfer reaction is efficient, gives good yields, and, avoids the necessity of dry conditions.

There are several noteworthy features of the reaction: (i) while the yield of π -allyl complex obtained from $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ is somewhat greater than that realized using $\text{Mn}(\text{CO})_5\text{Br}$ as the substrate, the presence of two phosphine ligands [i.e., $\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{Br}$] significantly retards reaction (69); (ii) the reactivity and selectivity of the ruthenium halides is markedly greater than that of the corresponding iron compounds [e.g., last two entries of Table VI (70)]; and (iii) phosphine substitution in the cyclopentadienylmetal complexes completely inhibits σ - or π -allyl formation [e.g., $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_n\text{Cl}(\text{PPh}_3)$ where $\text{M} = \text{Fe}, \text{Ru}, n = 1$; $\text{M} = \text{Mo}, n = 2$] (69). A possible pathway for the initial steps of the metal carbonyl halide–allyl halide reaction is given in Scheme 13 [illustrated for $\text{Mn}(\text{CO})_5\text{Br}$] and is similar to mechanisms already described for several other reactions. It is not yet known how the binuclear anion **63**, if formed, reacts with allyl halide to give the observed products.

TABLE VI
REACTION OF METAL CARBONYL HALIDES WITH ALLYL HALIDES, NaOH, AND $\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3^+\text{Cl}^-$

$\text{M}(\text{CO})_n\text{X}$	Allyl halide	Organic solvent	Temperature (°C)	Reaction time (h)	Product	Yield (%)	Reference
$\text{Mn}(\text{CO})_5\text{Br}$	$\text{C}_3\text{H}_5\text{Br}$	CH_2Cl_2	reflux	5	$\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_4$	80	68
$\text{Mn}(\text{CO})_5\text{Br}$	$2\text{-CH}_3\text{C}_3\text{H}_4\text{Cl}$	CH_2Cl_2	reflux	12	$2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_4\text{Mn}(\text{CO})_4$	48	68
$\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$	$\text{C}_3\text{H}_5\text{Br}$	CH_2Cl_2	reflux	1	$\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_3\text{PPh}_3$	90	68
$\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{Br}$	$\text{C}_3\text{H}_5\text{Br}$	CH_2Cl_2	reflux	1	$\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_2(\text{PPh}_3)_2$	trace	69
$\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_3\text{Br}$	$\text{C}_3\text{H}_5\text{Br}$	CH_2Cl_2	24	1	bis- $\pi\text{-C}_3\text{H}_5\text{Fe}(\text{CO})_2$	76	68
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$	$\text{C}_3\text{H}_5\text{Br}$	C_6H_6	45	8	$\pi\text{-C}_3\text{H}_5(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2$	95	68
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$	$\text{C}_3\text{H}_5\text{Br}$	CH_2Cl_2	24	5	$\sigma\text{-C}_3\text{H}_5(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_2$	75	68
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$	$\text{C}_3\text{H}_5\text{Br}$	C_6H_6	24	4	$\pi\text{-C}_3\text{H}_5(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})$	60	68
$\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$	$\text{C}_3\text{H}_5\text{Br}$	CH_2Cl_2	24	2	$\sigma\text{-C}_3\text{H}_5(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2$	36	68
					$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	30	
$\text{C}_5\text{H}_5\text{Ru}(\text{CO})_2\text{Cl}$	$\text{C}_3\text{H}_5\text{Cl}$	CH_2Cl_2	24	0.5	$\pi\text{-C}_3\text{H}_5(\text{C}_5\text{H}_5)\text{Ru}(\text{CO})$	80 ^a	70

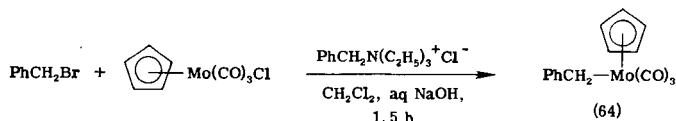
^a 1:1 exo-endo.



SCHEME 13

C. σ -Benzyl Complexes

Initial experiments by Gibson *et al.* (71) indicate phase-transfer catalysis to be a promising method for the synthesis of σ -benzyl complexes. Reaction of benzyl bromide with cyclopentadienylmolybdenum tricarbonyl chloride, under conditions similar to those described for the preparation of σ - and π -allyl complexes, afforded the σ -benzyl complex (64) in 89% yield. Use of benzyl chloride as substrate results in a considerably



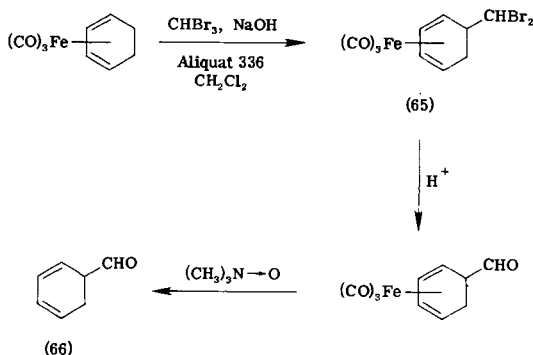
more sluggish reaction [4.5 h, 26% yield]. Complex 64 was previously synthesized in 67% yield by King and Fronzaglia (72) using rigorously dry conditions and a reaction period of 16 hours.

D. Diene-Iron Tricarbonyl Complexes: Dibromocarbene Insertion

The formation of dihalocarbene is one of the most useful phase-transfer processes developed in organic chemistry. The dihalocarbenes, once generated from haloform and base, can undergo addition or insertion reactions (3, 11, 12). If the double bond is complexed to a metal, addition by the carbene will not occur, but rather insertion into a saturated carbon-hydrogen bond will take place.

Diene-iron tricarbonyl complexes undergo C—H bond insertion reac-

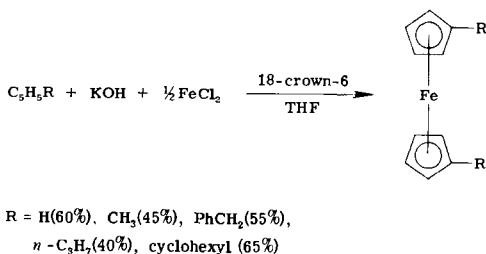
tions with dibromocarbene (73) to give dibromomethyl-substituted complexes in good yields (27–54%), particularly when compared with those reported for insertion reactions into most organic substrates (11, 12). An attractive feature of the insertion reaction is the fact that the reaction products [e.g., 65] are of considerable potential in organic synthesis [e.g.,



in the preparation of dienaldehydes (66) where the diene unit is not conjugated to the aldehyde].

E. Ferrocenes

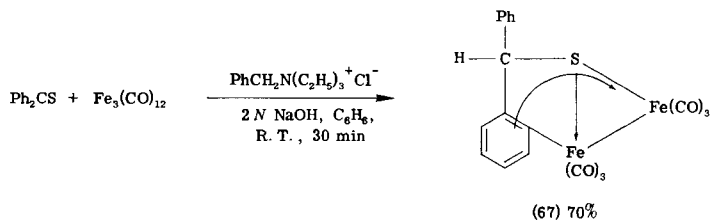
Metallocenes can be synthesized by solid–liquid phase-transfer catalysis (74). This mild reaction is most useful for the preparation of 1,1'-disubstituted ferrocenes. The method does not require alkali metals or anhydrous conditions, and reactions are complete in less than 1 hour.



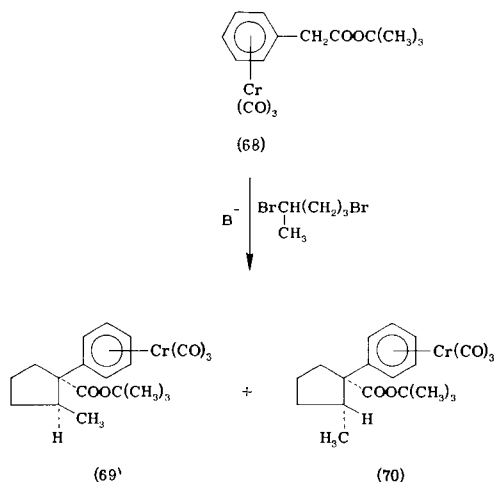
F. Arene Complexes

Sulfur–donor ligand ortho-metalated complexes [e.g., 67] are not only complexes of considerable structural interest, but are of genuine utility in

the synthesis of important organic compounds which are either difficult to prepare or inaccessible by other means (75, 76). The long reaction time required to synthesize the ortho-metalated complexes was undesirable in terms of their subsequent utility. The facile synthesis of these complexes can now be achieved by phase-transfer catalysis, and reaction work-up is easy as well (14).



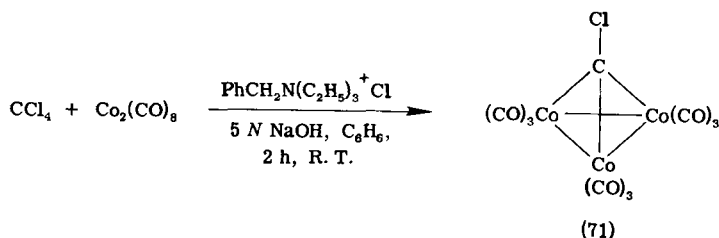
Chromium tricarbonyl complexes of arylacetic esters can be alkylated by the use of phase-transfer catalysis or sodium hydride in *N,N*-dimethylformamide (77). However, the yields obtained by the latter method are as good as or superior to those realized using phase-transfer techniques. Both methods give similar stereochemical results (e.g., **68** → **69** and **70**).



$\text{B}^- = 50\% \text{ NaOH, C}_6\text{H}_6, \text{C}_{18}\text{H}_{33}\text{N}(\text{CH}_3)_3^+ \text{Br}^-$	72	:	28 (45% yield)
$\text{B}^- = \text{NaH/DMF}$	74	:	26 (100% yield)

G. Clusters

Alkylidynetricobalt nonacarbonyl complexes are an interesting class of clusters (78). They can be synthesized by treatment of a tri- or tetrahaloalkane with cobalt carbonyl under phase-transfer conditions [e.g., **71**] (28). Partially or completely dehalogenated by-products were often isolated from these reactions.



V

CONCLUSIONS

Phase-transfer catalysis is a versatile and economical synthetic method in both stoichiometric and catalytic organometallic chemistry. New reactions await discovery, and many of those already reported require detailed mechanistic examination. The prospects for this area are excellent.

ACKNOWLEDGMENTS

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Redistribution Reactions on Silicon Catalyzed by Transition Metal Complexes

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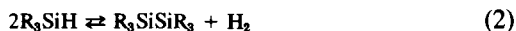
I

INTRODUCTION

Redistribution, or disproportionation, constitutes an important class of reactions in organosilicon chemistry. The reaction prototype is illustrated by Eq. (1) in which one or more substituents on silicon are mutually exchanged.

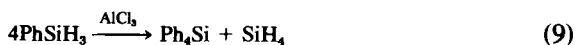
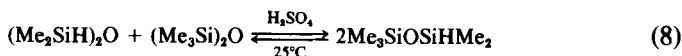
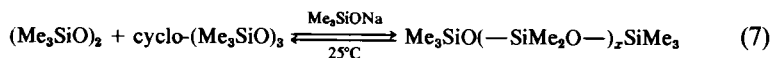
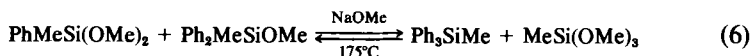


There are several excellent reviews on this type of reaction (1-4). In addition to the "pure" disproportionation shown in Eq. (1), other types of reactions [e.g., Eqs. (2-4)] represent generalized redistribution, as shown in Eq. (5).



Redistributions on silicon may be initiated by thermolysis or by catalytic activation at somewhat lower temperatures. Depending on the par-

ticular redistribution reaction, the catalysts may be strong bases [Eqs. (6) and (7)], strong protic or Lewis acids [Eqs. (8) and (9)] or transition metal complexes.

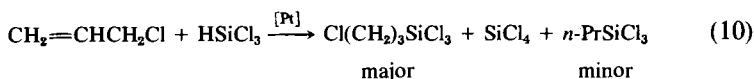


Catalysis of the redistribution by strong bases and strong acids is used on a large scale by the organosilicon industry and has been well covered in previous reviews (1-4). In spite of its extensive practical use, the mechanism of the AlCl_3 - or base-catalyzed redistribution of organic groups or hydrogen on silicon is not well understood. Presumably, when AlCl_3 is the catalyst, transient organoaluminum compounds are produced (2) and act as carriers of the organic moiety.

In the gas phase, methyl is transferred from $\text{Me}_n\text{SiH}_{4-n}$ to CH_3^+ almost as readily as hydrogen (5). In condensed phases, however, ligands may be arranged in order of decreasing mobility (1): (a) labile ligands—halogen, pseudohalogen, oxy, amino, and thio; (b) semilabile—hydrogen and silicon; and (c) nonlabile—alkyl and aryl.

This ordering generally holds for acid- or base-catalyzed redistributions, and it is usually possible to find conditions whereby ligands in one class may be scrambled without redistributing ligands in the less labile classes. Indeed, the silicon industry is based on the capacity to redistribute labile ligands [Eq. (7)] without scrambling the organic groups bonded to silicon.

Until relatively recently, less attention has been given to catalysis of redistribution reactions by transition metal complexes. Redistributions have been observed during the course of platinum-catalyzed hydrosilation; hence, the scrambling reaction can be a nuisance by decreasing the yield of desired hydrosilation products. A noteworthy example is the H/Cl exchange that occurs during the hydrosilation of allyl chloride [Eq. (10)].



However, recent results show that metal-complex-catalyzed redistributions may be very specific and thus synthetically useful.

This article will review the work done to date on transition metal-catalyzed redistributions on silicon. The authors believe that the review is reasonably exhaustive up to mid-1979. Excluded are transition metal salts that act primarily as Lewis acids (e.g., ZnCl_2 , TiCl_4 , or FeCl_3). The organization of material is arbitrarily arranged by class of silane: mono-, oligo-, and polysilanes, and siloxanes. Proposed mechanisms will be presented along with the descriptive material, but a critical discussion of mechanisms will be deferred to a separate section. Hydrosilation (6), although constituting a redistribution of bonds, will not be discussed except where some light is shed on the main theme of this article.

II

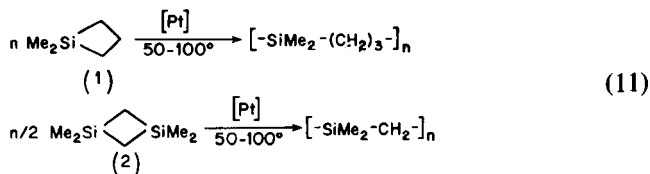
REDISTRIBUTIONS CATALYZED BY TRANSITION METAL COMPLEXES

A. Redistributions on Monosilanes

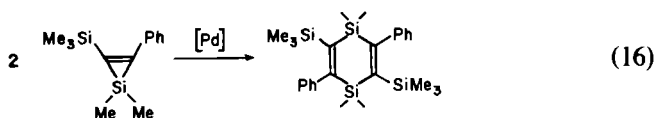
The material in this section is organized according to the exchanging groups on silicon: carbon for carbon (C/C), carbon for hydrogen (C/H), etc.

1. C/C Exchanges

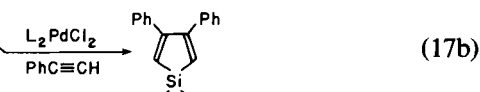
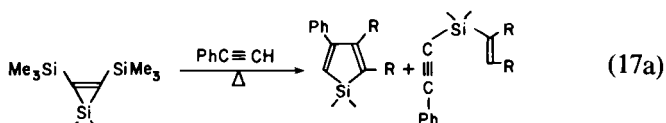
Weyenberg and Nelson (7) reported that the strained silacycles, 1,1-dimethyl-1-silacyclobutane (1) and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (2) undergo ring opening polymerization in the presence of platinum on carbon or chloroplatinic acid [Eqs. (11) and (12)].



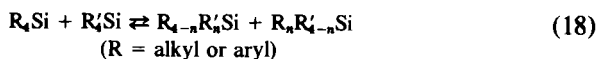
Bamford *et al.* (8) found that $\text{L}_2\text{Pt}_2\text{Cl}_4$ (L = alkene or phosphine) complexes were especially efficient catalysts for Eq. (12), giving gums with



reaction with phenylacetylene according to Eq. (17a); but with a catalytic amount of L_2PdCl_2 the reaction proceeds with complete exchange of the acetylenic moiety on the silylene [Eq. (17b)] ($\text{R} = \text{Me}_3\text{Si}$) (13b).



No reactions of the type shown in Eq. (18) have been reported to be catalyzed by transition metal derivatives. Sufficiently vigorous conditions (or the proper catalyst) have not been investigated or the ring strain inher-



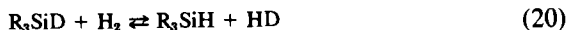
ent in the silacyclobutanes is a necessary condition for the rearrangement. In view of the fact that transition metals do insert into unstrained C—Si bonds (*vide infra*), we suspect that future work will reveal reactions of the type shown in Eq. (18).

2. C/H, H/D, and C/C Exchanges

In contrast to the relative paucity of examples of C/C exchange of the type shown in Eq. (18), C/H exchange, sometimes accompanied by C/C exchange, occurs readily when hydride ligands are present on silicon. The Si—H linkage, by virtue of its ability to add oxidatively to low-valent metals, thus attaching the silicon moiety to the metal center, appears to promote the exchange of other groups of silicon.

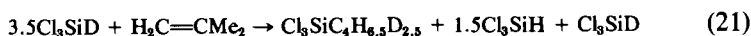
The reactions of silyl hydrides with low-valent metal complexes is a common method of preparing silyl derivatives of transition metals (14–16). However, relatively little work has been directed to the study of H/H (H/D) exchange. From the studies of Sommer *et al.* (17), it has been established that chloroplatinic acid, $(\text{C}_2\text{H}_4)_2\text{Pt}_2\text{Cl}_4$, $\text{Co}_2(\text{CO})_8$, $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$,

$R_3SiCo(CO)_4$, and the metals of the nickel triad catalyze H/D exchange typified by Eqs. (19) and (20).



By using chiral silyl hydrides, it was demonstrated that the exchanges occur with retention of configuration at silicon (17). Furthermore, these exchanges were extremely facile.

Ryan and Speier studied the hydrosilation of isobutylene with Cl_3SiD and found that the deuterium was exchanged with the hydrogen on the isobutylene (6, 18). The distribution of H/D was nearly random [Eq. (21)]



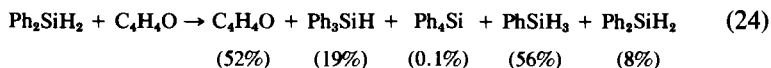
so that H/D exchange was occurring much faster than hydrosilation. These results on H/D exchange suggest that silyl metal hydrides are sources of low-valent, active complexes as a result of the equilibrium [Eq. (22)]



Although k_{-1} is expected to be very large, occasionally the coordinatively unsaturated species, L_nM , will be intercepted by another substrate (e.g., a Si—C bond) and give rise to some net reaction, such as redistribution of groups on silicon. Stated another way, one function of the Si—H bond is to generate an active catalyst from some catalyst *precursor* [e.g., Eq. (23)] (19). A fuller discussion of mechanistic implications is reserved for Section III.

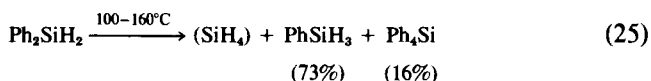


Gilman and Miles (20) were the first to observe C/H exchange during an attempted hydrosilation of furan with diphenylsilane. These workers found the products shown in Eq. (24) when diphenylsilane was heated at 100°C in a sealed tube with furan in the presence of catalytic amounts of chloroplatinic acid. When Ph_2SiH_2 alone was heated with chloroplatinic



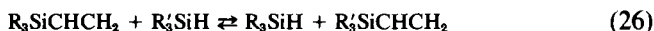
acid in an open system and volatiles allowed to escape through a bubbler, a spontaneously flammable gas (presumably silane, SiH_4) was produced. By allowing the silane to escape, the equilibrium among the various $Ph_{4-n}SiH_n$ compounds would be continually shifted. Hence, the pot residue should be rich in the more alkylated silanes. Rather surprisingly then,

these authors report the product distribution of the pot residue given in Eq. (25). A 73% yield of PhSiH_3 (based on Si!) is impossible unless hydro-

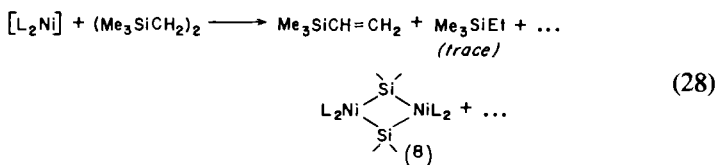
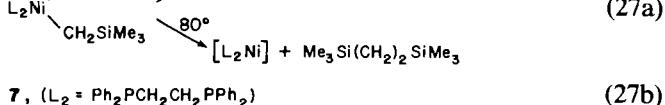
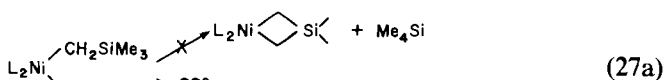


gen is abstracted from phenyl. Hence, either a typographical error is involved or the product was not correctly identified.

Vinyl/hydrogen exchange was observed when $\text{R}_3\text{SiCH}=\text{CH}_2$ was hydrosilated with $\text{R}_3'\text{SiH}$ with chloroplatinic acid as catalyst at 100°C (21). In addition to the expected $\text{R}_3\text{SiC}_2\text{H}_4\text{SiR}_3'$, the symmetric products $\text{R}_3\text{SiC}_2\text{H}_4\text{SiR}_3$ and $\text{R}_3'\text{SiC}_2\text{H}_4\text{SiR}_3'$ were also produced in yields of 1–5%. These symmetric products are explained as a result of vinyl/hydrogen exchange, followed by hydrosilation of the products of the redistribution reaction [Eq. (26)].

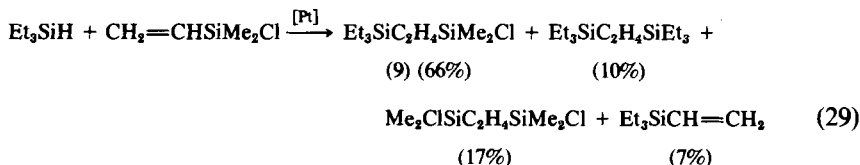


Recent results from our laboratories indicate another possible route to the symmetric products, $\text{R}_3\text{SiC}_2\text{H}_4\text{SiR}_3$ (22). During the course of our work on silylmetallacycles, we decomposed nickel complex **7** at 80°C in benzene. The decomposition proceeds cleanly to give 1,2-bis(trimethylsilyl)ethane and an unidentified nickel complex [either $\text{L}_2\text{Ni}(0)$ or the complex resulting from insertion into the *ortho* C—H bond of the phenyl groups on L]. When Eq. (27b) is approximately 90% complete, a slower rearrangement of the bis(silyl)ethane becomes apparent with the production of $\text{Me}_3\text{SiCH}=\text{CH}_2$ and a black, pyrophoric silylnickel complex believed to be **8** [Eq. (28)]. The production of a vinyl silane from the



bis(silyl)ethane, followed by hydrosilation, is thus an alternate mechanism to Eq. (26).

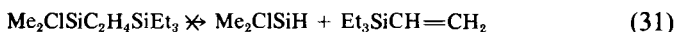
Pitt and Skillern (23) observed H/vinyl exchange during the addition of triethylsilane to vinyltrimethylchlorosilane catalyzed by chloroplatinic acid [Eq. (29)].



These authors also proposed the exchange shown in Eq. (30) to account for their observations.



A mixture of Et_3SiH and chloroplatinic acid did not rearrange **9** at 140°C , thus eliminating Eq. (31) as the source of the rearranged products in Eq. (29).

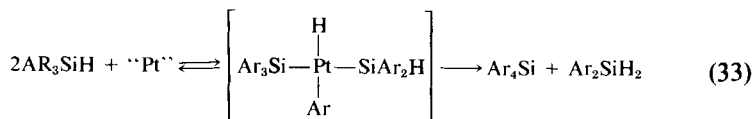


The same workers also investigated the disproportionation of tri-*p*-tolylsilane (23). When heated to 240°C in the presence of chloroplatinic acid, a mixture reported to be 7% Ar_2SiH_2 , 58% Ar_3SiH , and 35% Ar_4Si was produced ($\text{Ar} = p\text{-MeC}_6\text{H}_4$) [Eq. (32)]. The yields were determined by gas



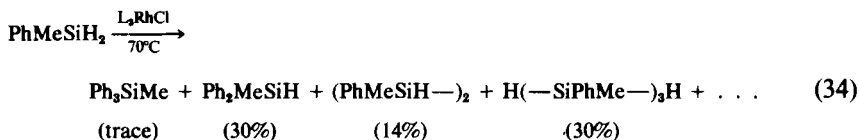
chromatography (GC) but must be incorrect since a mass balance does not obtain. Only about 33% of the hydrogen, but 120% of the tolyl groups, are accounted for by the reported yields. Our experience with response factors for silanes shows increased sensitivity to higher molecular weights with thermal conductivity detectors. Thus, the amount of Ar_4Si is probably overestimated, and the Ar_2SiH_2 underestimated vis-à-vis the Ar_3SiH . Even so, some hydrogen was probably lost as H_2 .

The complete lack of isomerization of the *p*-tolyl group during the disproportionation of Ar_3SiH is noteworthy. Pitt and Skillern proposed the mechanism shown in Eq. (33) to explain their results. These authors thus appear to be the first to write explicitly an oxidative insertion of a low-val-



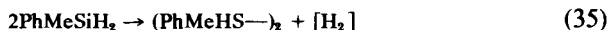
lent metal into the Si—C bond as the key step in transition metal-catalyzed redistributions on silicon. Note that one molecule of Ar_3SiH must add across the Si—H bond while the other must add to Pt across the Si—C bond.

Ojima *et al.* (24) studied the action of L_3RhCl ($\text{L} = \text{Ph}_3\text{P}$) on a series of silanes of the type R_2SiH_2 . Their results for the disproportionation of phenylmethylsilane are shown in Eq. (34).

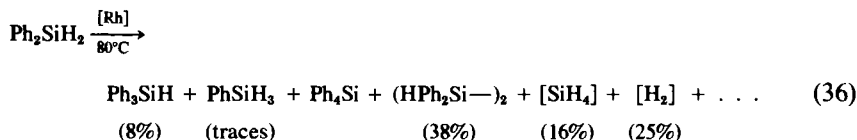


Epstein and Curtis (25) have also observed the disproportionation of phenylmethylsilane with 1 mol% Vaska's complex ($\text{L}_2\text{Ir}(\text{CO})\text{Cl}$) as catalyst at 40°C . Early in the reaction, some Me_2SiH_2 and Ph_2SiH_2 are detected. After completion of the reaction (99.6% of the PhMeSiH_2 consumed), no dihydridosilanes remain. The mixture contained PhMe_2SiH (11.8%), Ph_2MeSiH (30.6%), and Ph_3SiH (9.8%). No disilanes or trisilanes were detected with the Ir-based catalyst, and the yields of the monosilanes account for 100% of the Ph groups, 54% of the Me groups, 20% of the H, and 52% of the silicon originally in the PhMeSiH_2 . The groups not accounted for are in the ratio $\text{MeSi}_{1.04}\text{H}_{3.2}$, which corresponds to a 48% yield of MeSiH_3 plus a 2% yield of H_2 . The reaction conditions were such that the volatile $\text{MeSiH}_3/\text{H}_2$ mixture would have been lost. The reaction is being repeated on a high vacuum line to confirm that volatile silanes are being formed.

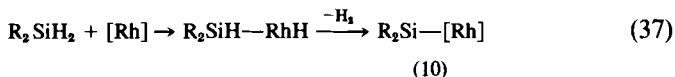
A similar treatment of the data of Ojima *et al.* shows that 0.66 mmol each of Me and Si and 3.3 mol of H are unaccounted for by the yields of products given in Eq. (32). These "missing" quantities correspond to a 26% yield each of MeSiH_3 and H_2 . The higher yield of H_2 in the Rh-catalyzed reaction vis-à-vis the Ir-catalyzed reaction is consistent with the formation of di- and trisilanes with the Rh catalyst. For each mole of Si—Si bonds formed, 1 mol of H_2 equivalent must be evolved [Eq. (35)]. The H_2 may enter into the general redistribution scheme before escaping from solution and hence may not appear exclusively as H_2 , but may also contribute to the hydrogen-rich silane fraction.



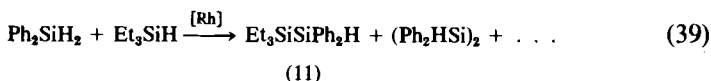
Similarly, Ojima *et al.* (24) observed the rearrangements of Ph_2SiH_2 given in Eq. (36). The products in brackets are those necessary for a mass balance, but not reported.



The mechanism proposed to explain the formation of polysilanes involves an α -elimination (26) to give a coordinated silylene or "silylenoid" complex (10) [Eqs (37–38)]. In support of this mechanism,

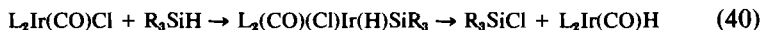


these authors "trap" the silylenoid species by running the disproportionation of Ph_2SiH_2 in the presence of Et_3SiH . An 8% yield of disilane **11** was obtained [Eq. (39)].



As discussed in Section III, however, the formation of **11** is not particularly strong evidence for silylenoid species **10**. Phenylsilane and diethylsilane also gave di- and trisilanes upon treatment with L_3RhCl (24).

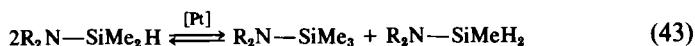
Under conditions where PhMeSiH_2 was completely converted to products with $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ as catalyst, the trialkylsilane PhMe_2SiH was essentially inert. After two days at 80°C , a 100% yield [based on the catalytic amount of $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ present] of PhMe_2SiCl , a trace of biphenyl, and <5% (based on Si) of Ph_2MeSiH were produced (25). The formation of the chlorinated silane is typical of the interaction of $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ with trialkylsilanes [Eqs. (40–41)].



Weyenberg and Nelson (7) were able to intercept the metallasilacyclopentane (**6**) with hydridosilanes RMe_2SiH thus giving C/H exchange on Si. The products are the telomers (**12**) shown in Eq. (42).



A methyl/hydrogen exchange was observed as side reaction during a chloroplatinic acid-catalyzed hydrosilation (6, 27). The anomalous products were rationalized by postulating the exchange shown in Eq. (43).



From the examples discussed, it is clear that organosilanes possessing Si—H bonds may undergo some rather remarkable rearrangements in the presence of transition metal complexes under very mild conditions. No systematic studies on mechanism, effect of various catalysts, or the relative migratory aptitudes of the various groups on silicon have appeared.

3. C/Cl and H/Cl Exchange

One of the first observed C/Cl exchanges on Si mediated by a transition metal complex was the stoichiometric cleavage of the alkyne-silicon bond shown in Eq. (44) (28). In the presence of ethanol, the Si—Cl bond is solvolyzed and an active Pt species is formed with the liberation of diethyl ketal. Under these conditions, the process is catalytic and Zeise's salt ($K[(C_2H_4)PtCl_3]$) is also an effective catalyst precursor [Eq. (45)].



A remarkably specific Me/Cl exchange was discovered by Beck and Benkeser (29). The reaction is typified by Eq. (46); the catalyst is chloroplatinic acid and typical conditions are 140°C/24 h. The data in Table I



illustrate the specificity for methyl transfer in the presence of diverse groups on silicon. No other reagent shows such specificity; hence, this method should find extensive use in synthesis of chlorosilanes.

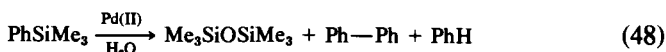
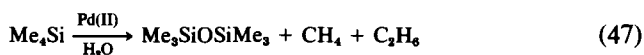
TABLE I
Me/Cl EXCHANGE PRODUCTS [Eq. (46)]^a

Reactant	Product (% yield)
Me ₄ Si	Me ₃ SiCl (97)
Me ₃ Si(CH ₃) ₆ SiMe ₃	ClMe ₃ Si(CH ₃) ₆ SiMe ₃ Cl (82)
Ph(CH ₂) ₂ SiMe ₃	Ph(CH ₂) ₂ SiMe ₂ Cl (81)
(<i>n</i> -Octyl)Et ₂ SiMe	(<i>n</i> -Octyl)Et ₂ SiCl (96)
PhSiMe ₃	PhMe ₂ SiCl (70)
(<i>n</i> -Octyl)SiMe ₂ Cl	(<i>n</i> -Octyl)SiMeCl ₂ (14)
(<i>n</i> -Octyl)SiMeCl ₂	No reaction
Me ₃ SiCl	Me ₂ SiCl ₂ (42)
(Me ₃ Si) ₂ O	(Me ₂ ClSi) ₂ O (50)

^a From Beck and Benkeser (29).

In contrast to the specific Me/Cl transfer, the higher valent halides and oxides of the early transition metals (e.g., WCl_6 , MoCl_3 , CoCl_3 , and ZrCl_4) stoichiometrically cleave the Si—Ph bond in PhSiMe_3 (30). The reaction mixtures were hydrolyzed and the resulting hexamethyldisiloxane analyzed. When the reaction of PhSiMe_3 with TiCl_4 was carried out at -30°C , a red solid was obtained to which Akhrem *et al.* ascribe the formula PhTiCl_3 (30). However, their evidence for this formulation is exceedingly weak.

Akhrem *et al.* (31) have also investigated the reaction of organosilanes with Pd(II) chlorides and observed the products shown in Eqs. (47) and (48). The Pd(II) is concurrently reduced to Pd metal.



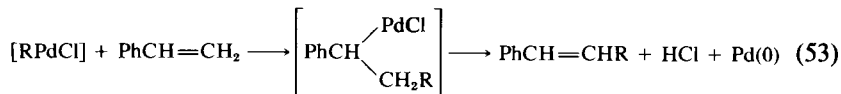
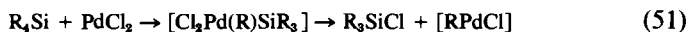
In solvents (e.g., THF or acetonitrile), Pd(II) salts are capable of transferring the organic group from Si to styrene [Eq. (49)]. The ease with which a



methyl group is transferred decreases in the order $\text{Me}_4\text{Si} > \text{Me}_3\text{SiEt} > (\text{Me}_3\text{Si})_2\text{NH} > (\text{Me}_3\text{Si})_2\text{O} > \text{Me}_3\text{SiCH}_2\text{Cl} > \text{Me}_3\text{SiPh} > \text{Me}_3\text{SiCl}$. The position of PhSiMe_3 in this series is artificial since this compound efficiently transfers the Ph group to styrene [Eq. (50)].



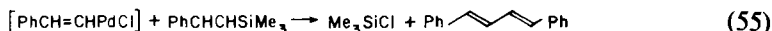
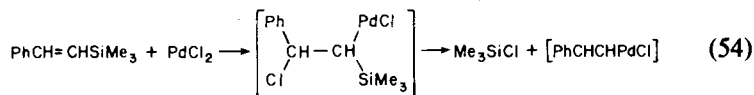
Equation (50), in conjunction with Eq. (48), demonstrates that transfer of methyl to Pd is simply not competitive with the transfer of Ph. The cleavage and transfer of the organic groups on silicon are thought to proceed through Eqs. (51–53).



Further research by Akhrem *et al.* (32) showed that in addition to PdCl_2 and Li_2PdCl_4 , the halides $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{RhCl}_3 \cdot 6\text{H}_2\text{O}$, and Na_2IrCl_6 were capable of cleaving methyl or phenyl groups from silicon similar to Eqs. (47–48). At 150°C , $\text{L}_2\text{Ir(CO)Cl}$, L_3IrCl and L_3RhCl ($\text{L} = \text{Ph}_3\text{P}$) were not

effective in cleaving phenyl but showed weak activity for cleaving methyl.

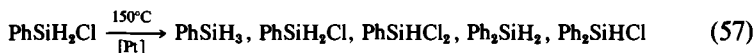
Weber *et al.* (33) observed the reductive coupling of β -trimethylsilylstyrene by PdCl_2 according to the Eqs. (54, 55).



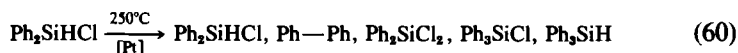
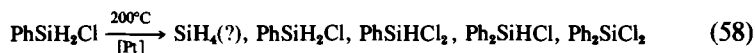
As was the case with C/C or C/H exchange, the reactivity of silicon compounds toward catalyzed H/Cl or C/Cl exchange increases markedly when hydride groups are present on silicon. Thus, refluxing EtSiH_2Cl for 15 min with chloroplatinic acid gives the conversion shown in Eq. (56) (34).



Also observed were the transformations shown in Eqs. (57–60). In these reactions, [Pt] is the platinum species derived from chloroplatinic acid and the reactants. The reaction shown in Eq. (57) was conducted in a sealed tube whereas that in Eq. (58) involved an open system which allowed volatiles (e.g., SiH_4) to escape. In addition to the products shown



(ratios: 1:8:12:11:13)



in Eq. (58), a large fraction of higher boiling materials was obtained but not characterized. The products observed in Eqs. (57–60) arise from H/Cl, C/H, and/or C/Cl exchange.

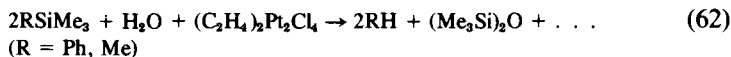
Kumada (35) describes a series of phosphinonickel(II) chlorides as being very effective catalysts for the H/Cl exchange in Eq. (61).



4. C/O Exchange

There are few reports of C/O exchanges on monosilanes, and in several of the reported instances, the reaction may proceed through C/Cl ex-

change, followed by hydrolysis or alcoholysis of the resulting silyl chloride (*vide supra*). For example, Mansuy *et al.* (36) report the stoichiometric hydrolysis of the C—Si bond according to Eq. (62). In the absence of



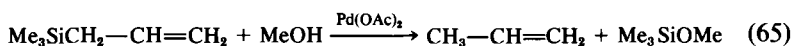
water, trimethylchlorosilane was produced. The hydrolysis was catalytic when mole ratios of $\text{RSiMe}_3/\text{Pt}_2/\text{H}_2\text{O}$ of 20:1:10 were employed.

Similarly, the vinyl group of trimethylvinylsilane is hydrolyzed by a catalytic amount of Zeise's salt $[(\text{C}_2\text{H}_4)\text{PtCl}_3]^-$ in moist acetone (37). In this study, the intermediate π -complex formed $[(\text{Me}_3\text{SiC}_2\text{H}_3)\text{PtCl}_3]^-$ from the displacement of ethylene on Zeise's anion by the vinylsilane was isolated and shown to hydrolyze to Zeise's anion and hexamethyldisiloxane in moist acetone [Eqs. (63–64)].



A derivative of Zeise's salt $[\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{toluidene})]$ formed by displacement of a chloride by toluidene was found effective in promoting the hydrolysis of phenyl or methyl groups in the presence of aqueous trifluoroacetic acid (38).

Palladium salts promoted the cleavage of the allyl group in allyltrimethylsilane, according to Eq. (65).



The complex Li_2PdCl_4 and allyltrimethylsilane yielded the products (% yield based on Si and Pd, respectively): $(\pi\text{-allyl})_2\text{Pd}_2\text{Cl}_2$ (32, 81%), Me_3SiOMe (75, 188%), $(\text{Me}_3\text{Si})_2\text{O}$ (25, 63%), propene (56, 140%) (reaction in methanol); and $(\pi\text{-allyl})_2\text{Pd}_2\text{Cl}_2$ (18, 56%), $(\text{Me}_3\text{Si})_2\text{O}$ (94, 291%), and propene (59, 183%) (reaction run in moist THF) (39).

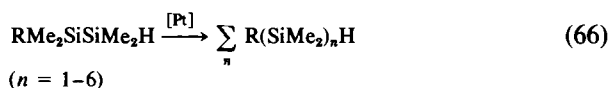
B. Redistributions on Di- and Polysilanes

1. Reactions of Hydridodisilanes ($\text{R}_3\text{SiSiR}_2\text{H}$)

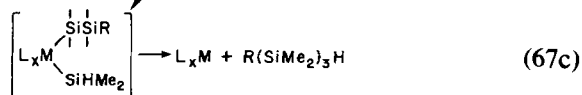
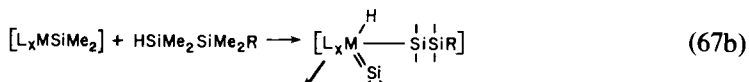
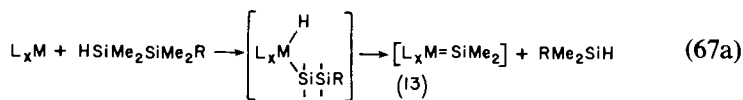
The redistribution reactions of hydridodisilanes of the type $\text{R}_3\text{SiSiR}_2\text{H}$ are more varied than those of the corresponding monosilanes. This phenomenon is attributed to two factors. First, there are two possible Si sites for exchange instead of one; and second, there are two very reactive cen-

ters on *one* silicon—namely, the Si—Si and Si—H bonds. In actual practice, it appears that the second factor is responsible for most of the increased complexity in that double displacement on one center gives hydrido disilanes a “silylenoid,” R_2Si , reactivity. Kumada has recently reviewed some skeletal transformations of polysilanes including acid-, base-, and some metal complex-catalyzed reactions (40).

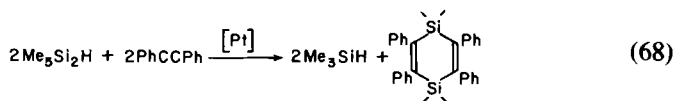
Difficulties (41, 42) associated with the use of pentamethyldisilane in hydrosilations catalyzed by usual metal complex catalysts led Yamamoto *et al.* to study the interaction of penta- and tetramethyldisilanes with transition metal complexes (43). Bis(phosphine)platinum chlorides effectively catalyzed the redistribution in Eq. (66) ($R = Me, H$). Yamamoto *et al.*



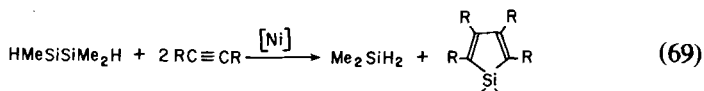
postulated that the redistribution [Eq. (66)] proceeds by way of a metal-silylene ($M = SiR_2$) formed by the α -elimination of $RSiMe_2H$ [Eq. (67a)]. The metal-silylene then “inserts” into the Si—H bond of a second disilane [Eq. (67b)]. Transfer of H and silicon to the silylene (insertion plus reductive elimination) gives the next higher homolog and regenerates the active catalytic species [Eq. (67c)].



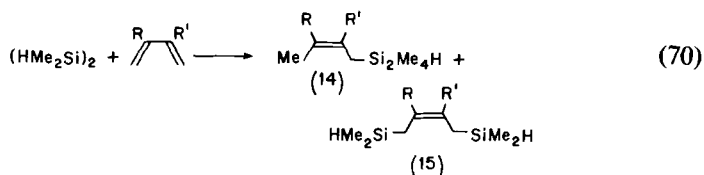
Some support for the existence of the silylene species **13** comes from various trapping experiments with acetylenes. Depending on relative rates, **13** may react preferentially with another disilane or with an added acetylene. With platinum catalysts (L_2PtCl_2 is the catalyst precursor) and unactivated acetylenes, **13** is preferentially intercepted by the acetylenes, yielding eventually the disilacyclohexadiene [Eq. (68)] (44). With a nickel



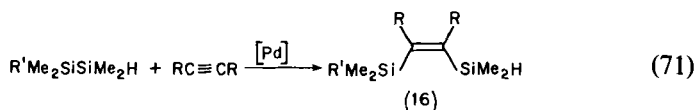
catalyst precursor, L_2NiCl_2 , and tetramethyldisilane, the metal silylene is again intercepted by the acetylene, but the intermediate(s) leads to a sila-cyclopentadiene in high yield [Eq. (69)] (45). The reaction of tetramethyl-



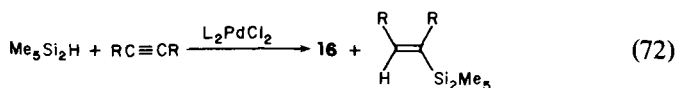
disilane with conjugated dienes in the presence of the same nickel catalyst leads to 1,4-hydrosilation (14) and to a product (15) which is the result of the cleavage and 1,4-addition of the Si—Si bond to the diene [Eq. (70)] (45).



A similar addition of the Si—Si bond to the “activated” acetylene $RC\equiv CR$ ($R = MeO_2C-$) is observed with $(Et_3P)_2PdCl_2$ as the catalyst precursor [Eq. (71)] (46). Changing the phosphine to triphenylphosphine

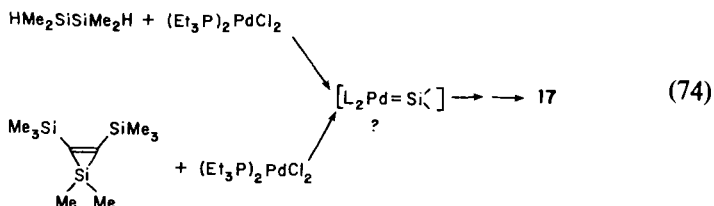
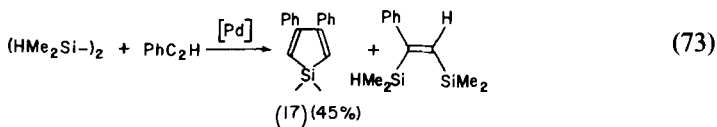


(L) gave hydrosilation in addition to 16 [Eq. (72)]. With the unactivated



acetylene $PhC\equiv CH$, the products shown in Eq. (73) result, with $(Et_3P)_2PdCl_2$ as catalyst (46). Compound 17 is significant in that it has the same structure as the sila-cyclopentadiene obtained via Eq. (17b). Hence, a common intermediate is produced [Eq. (74)].

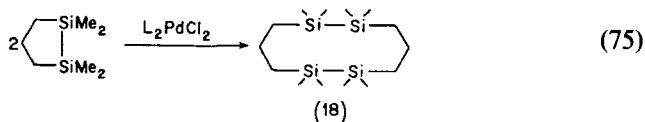
Thus, the metal-catalyzed reactions of several silicon species with acetylenes clearly show evidence for the generation of metal silylene species as well as Si—Si and Si—H cleavage. The nature of the metal catalyst, its ancillary ligands, and the nature of the substrate determine the ultimate product distribution. It is probable that certain silicon species are com-



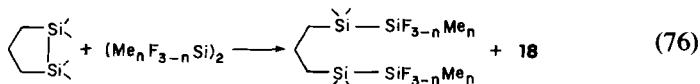
mon to all these reactions (see Section III). Also, as was the case with redistributions on monosilanes, the presence of a Si—H bond in the molecule greatly facilitates rearrangements catalyzed by transition metals.

2. Reactions of Cyclic Disilanes

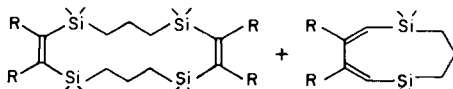
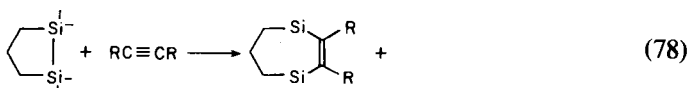
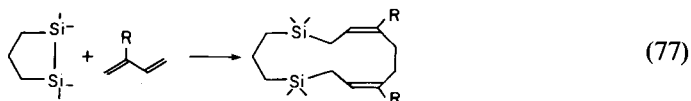
Introducing strain into the Si—Si bond renders it more reactive to reactions with transition metal species. Thus, Tamao *et al.* (47) have observed the redistribution of Si for Si shown in Eq. (75). Fluorine substituents on



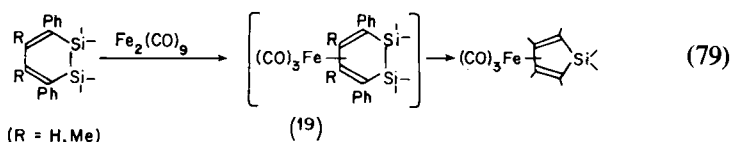
silicon also activate the Si—Si bond so that the metathesis shown in Eq. (76) was also observed (47). The order of reactivity of the fluoromethyl-disilanes decreased according to: $\text{F}_2\text{SiSiF}_2 > \text{FSiSiF}_2 > \text{F}_2\text{SiSi} > \text{FSiSi}$.



As was done in the metal-catalyzed redistributions of the hydridodisilanes, the active metal-silyl species can be intercepted by other substrates (e.g., acetylene) thus leading to synthetically useful reactions. For example, the cyclic disilanes react with acetylenes and dienes to give a variety of products, depending on the metal catalyst, the substrate, etc. (48–50) [Eqs. (77–78)].

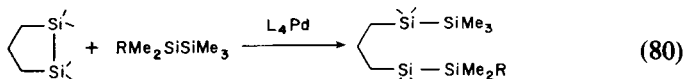


A Si/C redistribution was observed by Nakadaira *et al.* (51) in the novel ring contraction of [Eq. (79)]. The uncomplexed disilacyclohexadiene does not rearrange under the reaction conditions.

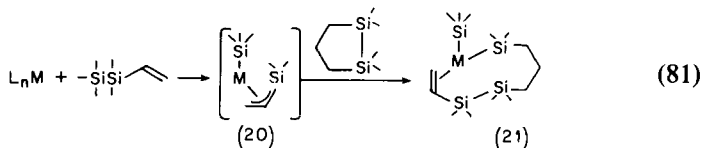


3. Reactions of Alkenyl Disilanes

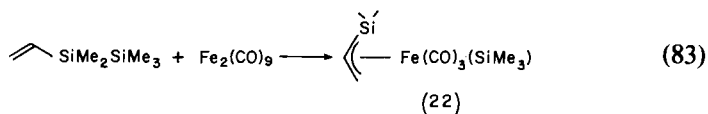
The presence of an unsaturated group on the Si—Si functionality also enhances its activity toward cleavage by transition metal complexes. Thus, Sakurai *et al.* (52) observed the disproportionation shown in Eq. (80) when R = —CH=CH₂ or —C≡CH. Hexaalkyldisilanes are inert



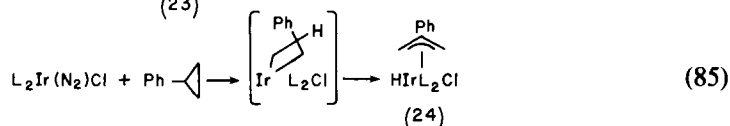
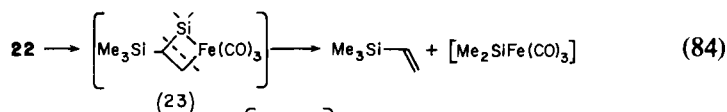
under similar conditions. The proposed mechanism invokes the formation



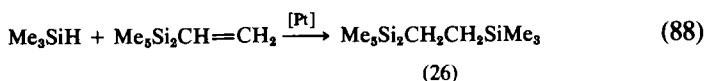
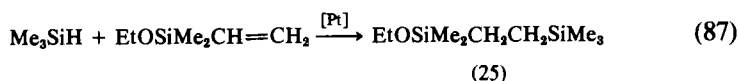
of a π -silaallyl complex (**20**). A stable π -silaallyl complex (**22**) is claimed to form from vinylpentamethyldisilane and $\text{Fe}_2(\text{CO})_9$ (**53**).¹ When decom-



posed thermally or photolytically, complex **22** forms vinyltrimethylsilane (**51**), possibly via the mechanism shown in Eq. (84). The transfer of silyl from Fe to the β -carbon is the reverse process of β -hydrogen transfer to metal postulated for the formation of **24** (**54**). The scission of the four-membered metallacycle (**23**) is analogous to the proposed decomposition mechanisms of metallacyclobutanes in the olefin metathesis reaction (**55**–**57**).



Vinylpentamethyldisilane undergoes a facile, chloroplatinic acid-catalyzed ethanolysis according to Eqs. (86–88) (**42**).



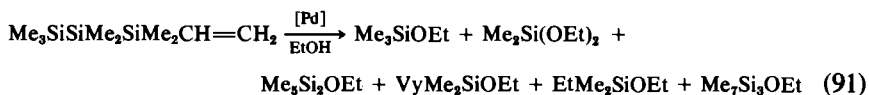
The final observed products are **25** and **26**. Hexamethyldisilane is inert under these reaction conditions, again illustrating the activating influence

¹ Radnia and McKennis (**53a**) present evidence that the correct structures for the complexes claimed to be **22** are actually the disilanylvinyln tetracarbonyl adducts, $(\text{R}_3\text{SiSiR}'_2\text{CH=CH}_2)\text{Fe(CO)}_4$, bonded in the normal η^2 -vinyl manner. The NMR nonequivalence of the R' groups arises from their diastereotopic nature. Complex **22** may still be an intermediate in the decomposition reaction (**84**).

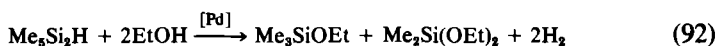
of the vinyl substituent. With PdCl_2 as catalyst, hydrogenation rather than hydrosilation was observed. Following Eq. (86) as the first step, the resultant silanes are then alcoholized under catalysis by the Pd species, giving as final products Me_3SiOEt [Eq. (89)] and RMe_2SiEt [Eq. (90)] ($\text{R} = \text{Me}_3\text{Si}$, EtO).



The PdCl_2 -catalyzed ethanolysis of 1-vinylheptamethyltrisilane proceeds according to Eq. (91). These products all arise as a consequence of



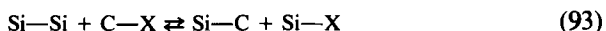
a series of reactions analogous to Eqs. (86), (89), and (90). Interestingly, $\text{Me}_3\text{Si}_2\text{H}$ solvolyzes according to Eq. (92), but $\text{Me}_3\text{Si}_2\text{OEt}$ is inert to further solvolysis (42).



From these examples, it appears that Si—Si bonds are relatively unreactive unless activated. Activation is achieved by fluoro, hydrido, or alkenyl substituents on the disilane, or by incorporating the Si—Si unit in a strained ring.

4. Reactions of Disilanes with Organic Halides

The exchange typified by Eq. (93) is potentially of industrial importance. Di- and polysilanes are by-products of the direct synthesis of



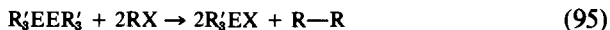
Me_2SiCl_2 from methyl chloride and elemental silicon. Hence, a facile method of transforming these by-products into new and useful organosilanes is desirable. Atwell and Bokerman (58) report that the reaction shown in Eq. (94) can be catalyzed by a variety of means, and that the reaction is particularly favored when RX is an allyl halide.



Aryl chlorides and bromides are reported to react with Me_6Si_2 , $(\text{ClMe}_2\text{Si})_2$, and $(\text{Cl}_2\text{MeSi})_2$ at approximately 140°C with $(\text{Ph}_3\text{P})_4\text{Pd}$ as the catalyst (59). Yields are high—in 20 h the conversions were as high as

90–100% with aryl bromides. Chlorobenzene requires a higher temperature (170°C) for comparable reactivity but *p*-O₂NC₆H₄Cl reacts at 140°C. Phenyl iodide fails to react, presumably because the adduct [L₂Pd(I)(Ph)] is too stable.

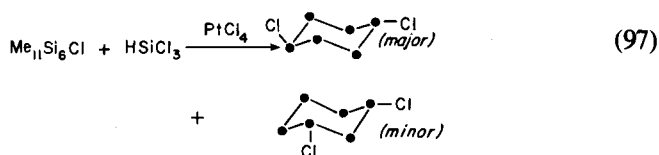
Another pair-wise exchange between organic halides and disilanes is possible and is shown in Eq. (95). This type of exchange is more pronounced



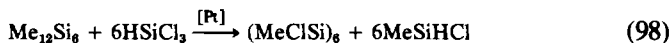
for the heavier group IV congeners (E = Sn) or when R = benzyl (60).

5. Reactions of Polysilanes

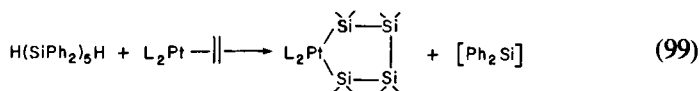
Relatively little work has appeared on the higher silanes. West (61) reports that the application of Beck and Benkeser's (29) reaction [see Eq. (46)] to dodecamethylcyclohexasilanes gives the products shown in Eqs. (96) and (97) (61). It thus appears that the first chlorine introduced exerts a



directive effective on the second. Peter and Hengge (62) report the preparation of (MeClSi)₆ by this method [Eq. (98)]. These reactions [Eqs. (96–98)] again illustrate the synthetic utility of this remarkably specific exchange.



A redistribution of diphenylsilyl groups apparently occurs when L₂Pt(C₂H₄) is treated with decaphenylpentasilane, 1,5-H(SiPh₂)₅—H. Instead of the expected L₂Pt(SiPh₂)₅, the five-membered metallacycle in Eq. (99) results (63).



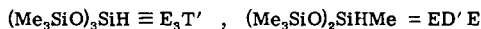
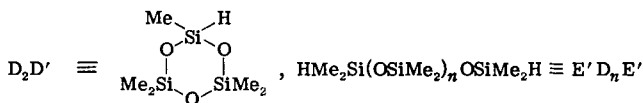
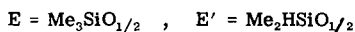
C. Redistributions of Siloxanes

In redistribution reactions catalyzed by transition metal complexes, di- or polysiloxanes are expected to share some characteristics of both monosilanes and di- or polysilanes. Similarities to the former are expected since the very reactive Si—Si bond is replaced by the less reactive Si—O bond, and to the latter because there are two or more exchangeable sites in the molecule.

At the outset of this discussion, it is perhaps worth noting that there is a considerable difference between the lability of groups on silicon toward redistribution catalyzed by acids or bases (see Section I) and transition metal complexes. Thus, oxy substituents are classified as "labile" and hydrogen as "semi-labile" toward acid- or base-catalyzed redistribution, whereas the reverse is usually the case with transition metal-catalyzed redistributions. Thus, these two sets of catalysts are complementary in their capacity to labilize the various substituents on silicon.

1. Notation

A convenient notation has been developed for depicting siloxane structures in an abbreviated manner. This notation is based on the functionality of the silicon center. Common usage has M, D, T, and Q groups which are, respectively, $\text{Me}_3\text{SiO}_{1/2}$, Me_2SiO , $\text{MeSiO}_{3/2}$, and SiO_2 (i.e., mono-, di-, tri-, and tetrafunctional groups). Since we have used "M" to denote a metal species, we have denoted the monofunctional group by "E" (end group). A prime indicates a hydrogen for methyl substitution. The following example summarizes the notation and illustrates its use. To conserve space, this notation will be used except where it would obscure the nature of the reaction under discussion.



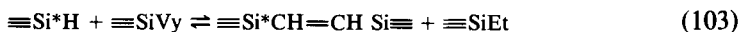
2. Reactions of Siloxanes

Redistributions on a siloxane was first observed as a side reaction during the chloroplatinic acid-catalyzed hydrosilation of 2-hexene with the heptamethyltrisiloxane, R_2MeSiH ($R = Me_3SiO$) (64). In addition to the expected product [R_2MeSi (*n*-hexyl)], $SiMe_2R$ (*n*-hexyl) and R_3SiH were also obtained.

These results led Stober *et al.* to postulate the Me_3SiO/Me exchange shown in Eq. (100). No redistribution was observed during the faster hydrosilation of 1-hexene.



With certain transition metal complex catalysts, a multitude of products were observed during the hydrosilation of $Me_3SiCH=CH_2$ with R_2MeSiH ($R = Me_3SiO$) (65). The products could be explained as a result of four concurrent reactions: R/Me exchange [Eq. (100)], vinyl/ H exchange [Eq. (101)], hydrosilation [Eq. (102)], and dehydrogenative double hydrosilation [Eq. (103)] (65). Products arising from Me/H exchange were not observed, and Os- and Ir-based catalysts gave the highest degree of disproportionation products. In order to explain the products with H_2IrCl_6 as catalyst, another disproportionation beyond Eq. (100) was postulated [Eq. (104)].



When R_2MeSiH (ED'E) was heated to approximately 120°C with 1% H_2IrCl_6 (no olefin present), the products (mol%) were reported as Me_3SiH (49%), RMe_2SiH (13%), R_2MeSiH (10%), and R_3SiH (28%). In the shorthand notation, these results are summarized in Eq. (105).



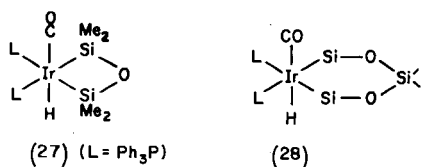
Curtis and Green observed the disproportionation of tetramethyldisiloxane, $HMe_2SiOSiMe_2H$, or $E'E'$, catalyzed by $L_2Ir(CO)Cl$ or L_3RhCl precursors (66). At shorter reaction times, gas-chromatographic/mass-spectroscopic (GC/MS) analysis shows a preponderance of the linear oligomers $E'D_nE'$ [Eq. (106)].



Equation (106) represents an $\text{Me}_2\text{HSiO}/\text{H}$ exchange and is remarkably similar to the disproportionation of $\text{HMe}_2\text{SiSiMe}_2\text{H}$ that occurs via an $\text{HMe}_2\text{Si}/\text{H}$ exchange [see Eq. (67)]. From the relative amounts of $\text{E}'\text{D}_n\text{E}'$ as a function of n , it appeared that the oligomers formed sequentially, with $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ as catalyst precursor. This was verified by the "cross" exchange shown in Eq. (107). Equation (107) corresponds to the removal of a Me_2SiO (D) unit from $\text{E}'\text{E}'$ and insertion of the D unit into the $\text{Si}-\text{H}$ bond of $\text{E}'\text{DE}'$ or, alternatively, as an exchange of Me_2HSiO on $\text{E}'\text{E}'$ for an H on $\text{E}'\text{DE}'$.



The catalytically active complex formed from $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ and $\text{E}'\text{E}'$ was isolated and shown to be the metallacyclodisiloxane, **27** (Fig. 1) (66, 67). The reaction of $\text{E}'\text{DE}'$ and $\text{L}_2\text{Ir}(\text{CO})\text{Cl}$ yielded the six-membered ring



complex **28**. Under conditions where $\text{E}'\text{E}'$ disproportionates [Eq. (106)] under the influence of **27**, $\text{E}'\text{DE}'$ alone showed no reactivity (at slightly higher temperatures, $\text{E}'\text{DE}'$ does slowly redistribute—*vide infra*).

Thus, the availability of the four-membered metallacycle in the catalytic cycle greatly enhances the rate of disproportionation of tetramethyldisiloxane. To account for the catalytic activity leading to the oligomeric

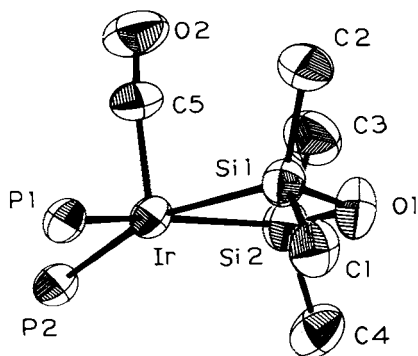
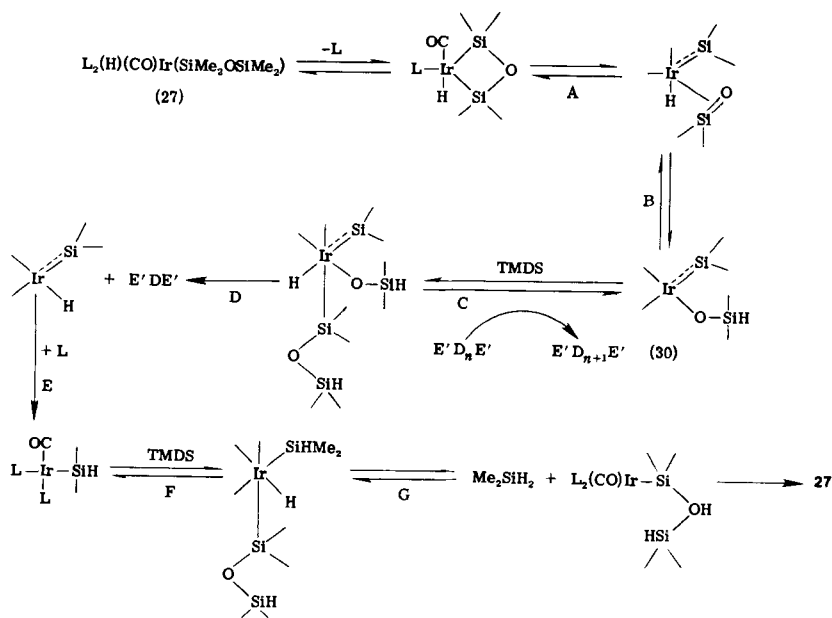
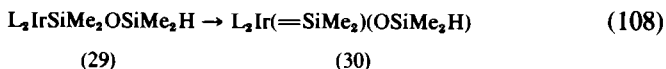


FIG. 1. Inner coordination sphere of $(\text{Ph}_3\text{P})_2\text{Ir}(\text{H})(\text{CO})(\text{SiMe}_2\text{OSiMe}_2)$. The hydride ligand (and not shown) occupies the vacant site trans to the carbonyl.



SCHEME 1. Proposed mechanism for the SiO/H redistribution of tetramethyldisiloxane ($E'E'$).

siloxanes, Curtis and Green postulated a ring scission to give a coordinated silanone (Step A, Scheme I). A rapid hydride shift to the silanone (Step B) generates the silylene species, $L_2Ir(=SiMe_2)(OSiHMe_2)$. This process is equivalent to an α -elimination of $-OSiHMe_2$ from a coordinatively unsaturated, Ir(I) species, **29** [Eq. (108)]. In effect, the ring forma-



tion is postulated to assist the α -elimination process by introducing strain into the Si—O bond. Some support for this hypothesis comes from the crystal structure of **27** (67). The SiOSi angle is 99.8° , a value which is considerably lower than the SiOSi angles in unstrained siloxanes (130 – 150°). The large SiOSi angle has been ascribed to the effects of (p–d) π -bonding between Si and oxygen. Hence, a forced reduction of the SiOSi angle should lead to decreased (p–d) π -bonding and to a lengthening of the Si—O bond. In fact, the Si—O bond in complex **27** is $1.684(8) \text{ \AA}$, significantly longer than the normal 1.63 – 1.65 \AA found in unstrained structures. The enhancement of the α -elimination process in **27** may result in part from angle strain in the four-membered ring.

The mechanism in Scheme 1 accounts for the sequential formation of oligomers. The tetramethyldisiloxane ($E'E'$ or TMDS) adds to **30** in Step C. Subsequent reductive elimination (Step D) produces the trimer $E'DE'$. As the concentration of $E'DE'$ increases, the trimer can oxidatively add to **30** in Step C, producing the tetramer $E'D_2E'$, and so on.

With longer reaction times, new products other than the oligomers $E'D_nE'$, begin to appear. We have now established that these new products are the result of secondary rearrangements of the oligomers (25, 68). A typical GC trace is shown in Fig. 2, and Table II lists the products through Si_6 that have been identified in the L_3RhCl - or $L_2Ir(CO)Cl$ -catalyzed redistribution of $HMe_2SiOSiMe_2H$ ($E'E'$). The higher oligomers [$E'D_nE'$ ($n > 6$)] are also apparent in the GC traces, along with their isomers and corresponding rearrangement products.

The redistributions of pentamethyldisiloxane EE' and hexamethyltrisiloxane $E'DE'$ were reinvestigated using our computerized data system. The purpose of these experiments was to gain some insight into the

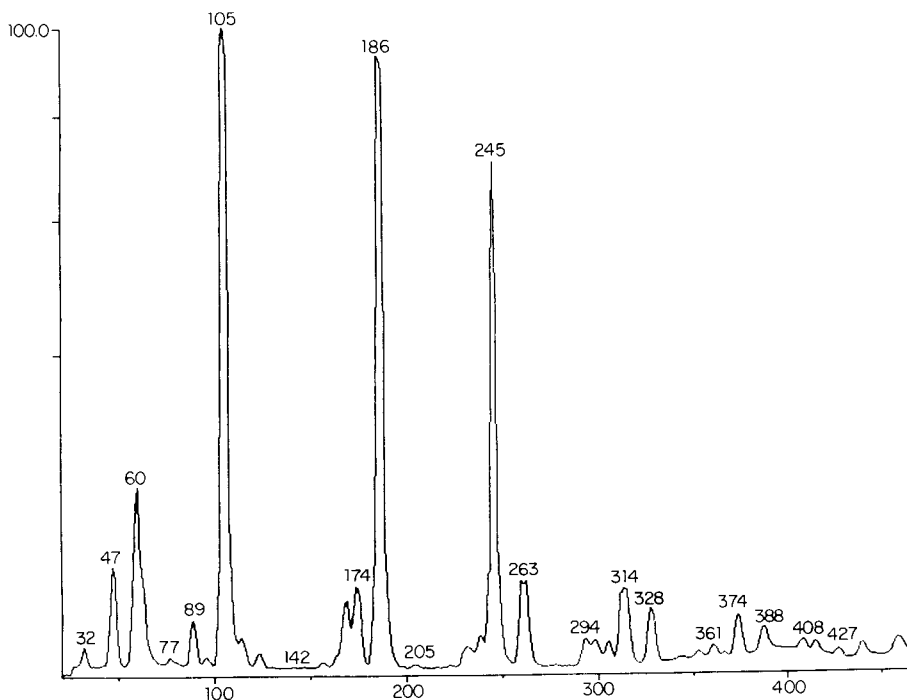


FIG. 2. Typical ion current GC trace of the reaction mixture resulting from the disproportionation of tetramethyldisiloxane ($E'E'$).

TABLE II
 REDISTRIBUTION PRODUCTS OF TETRAMETHYLDISILOXANE (E'E')

	Products ^a	Area %	Products ^b	Area %
Si ₁	PhSi ₂ OMe ₄ H ^c	1	PhSi ₂ OMe ₄ H ^c	2
	PhSiMe ₂ H ^c	1.1	PhSiMe ₂ H ^c	n.a.
Si ₃	E'DE'	60	E'DE'	9
	(ED'E)	0.1	E'De	1
	E'D'E'	0.1	E'D'E'	5
	D ₃	0.5	D ₃	0.8
	D ₂ D'	0.4	D ₂ D'	0.8
			+ 3 others	1
Si ₄	E'D ₂ E'	21	E'D ₂ E'	13
	E'DD'E'	1.4	E'DD'E'	13
	D ₄	tr	E'D ₂ 'E	1.3
	D ₃ D'	1.1	D ₄	4
			+ 2 others	2
Si ₅	E'D ₃ E'	2.0	E'D ₃ E'	8
	E'D ₂ D'E	6.0	E'D ₃ D'E	10
	E'D ₂ 'DE	0.2	E'D ₂ 'DE	4
	E'D ₃ E	0.1	E'D ₂ 'DE'	0.1
Si ₆	E'D ₄ E'	2.0	E'D ₄ E'	23
	+ 12 others	1.8	D ₆ (?)	2
			+ 9 others	3.6

^a 4 ml E'E', 2 ml benzene, 120 mg L₂Ir(CO)Cl, 60°C. Reaction time = 48 h.

^b 6 ml E'E', 4 ml benzene, 120 mg L₃RhCl, 60°C. Reaction time = 17 h. Area % were determined on a computerized plotter/integrator using a thermal conductivity detector.

^c These products are formed by reaction with the benzene—see text.

scrambling reactions observed on the oligomers E'D_nE' at longer reaction times. The siloxanes EE' and E'DE' cannot form the four-membered metallacycle necessary for the postulated strain-enhanced α-elimination mechanism (Scheme 1). Even so, both EE' and E'DE' do undergo redistribution in the presence of Vaska's complex, but at a much slower rate than the oligomerization reaction of E'E'. The redistribution products of EE' and E'DE' are summarized in Tables III and IV, respectively. These products are the result of every possible exchange, Me/H, SiO/Me, and SiO/H. The reaction conditions were such that H₂ or volatile silanes (e.g. MeSiH₃ or Me₂SiH₂) would have been lost.

In the EE' reaction (Table III), the Me/H exchange leading to hexamethyldisiloxane (EE) should also give the unsymmetric tetramethyldisiloxane, **31** (R = Me₃SiO—) [Eq. (109)]. However, we have shown that

TABLE III
REDISTRIBUTION PRODUCTS OF PENTAMETHYLDISILOXANE (EE')^a

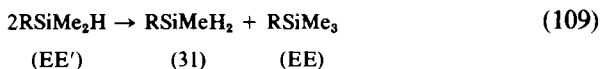
Product	%	Analysis ^b	Product	%	Analysis ^b
Me ₃ SiH	0.6	1	E ₃ T	<1	1
EE	3.5	1	ED ₃ E	4.4	2
RMe ₂ SiCl ^c	0.3	1	E ₄ Q	<1	1
ED'E	74.6	2	ED ₃ E	<1	1
EDE	5.1	2	ED ₃ D'E	<1	1
E ₃ T'	5.0	2	PhSiMe ₂ R ^{c,d}	<1	1
ED'DE	6.7	2			

^a Catalyzed by 1–2 mol% Vaska's complex at 60°C. Product percentages are area % of total product.

^b Analysis method: (1) retention time and comparison of the mass spectrum to an authentic sample or to a spectrum on the computer library; (2) as in (1) plus preparative GC and analysis of ¹H- and/or ¹³C-NMR spectra.

^c R = Me₃SiO; the chlorinated products arise from H/Cl exchange with the catalyst precursor.

^d Phenyl group from benzene solvent—see text.



dihydridosilanes undergo very rapid disproportionations so that any **31** produced would be entirely converted according to Eqs. (110) or (111).

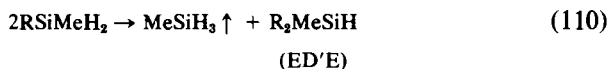


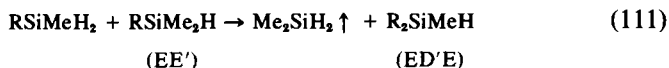
TABLE IV
REDISTRIBUTION PRODUCTS OF HEXAMETHYLTRISILOXANE (E'DE')^a

Product ^b	%	Product	%
E'DE	4.4	E'DD'DE ^c	7.9
EDE	0.6	E'D ₃ E'	13.6
EDE' ^{Cl}	8	E'D ₃ D'E ^c	3.7
D ₃ D'	31.6	E'D ₄ E'	6.0
E'D ₃ E'	24.1		

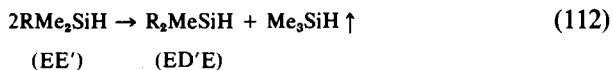
^a E'DE' 2.04 M in PhH with ~200:1 L₄Ir(CO)Cl as catalyst.

^b A superscript "Cl" indicates methyl replaced by Cl, i.e., EDE'^{Cl} = Me₃SiOSiMe₂-OSiMe₂Cl. This compound is formed by H/Cl exchange of the substrate with the catalyst precursor.

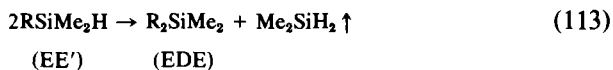
^c As indicated or one of the isomeric oligomers, e.g., E'DD'D'E. The analyses of these mixtures by preparative GC and NMR have not been completed.



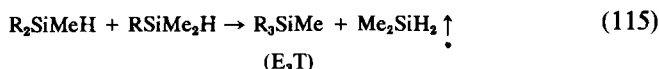
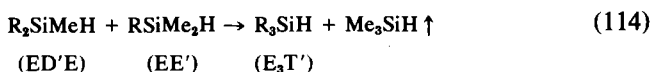
The primary product in the redistribution of EE' is ED'E, and this can also form from SiO/Me exchange [Eq. (112), R = Me₃SiO]. The EDE



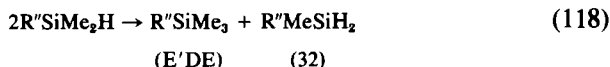
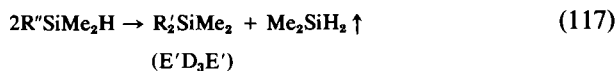
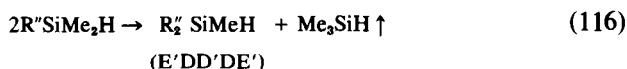
could come from Me/H exchange on ED'E or, more likely, from SiO/H exchange [Eq. (113)].



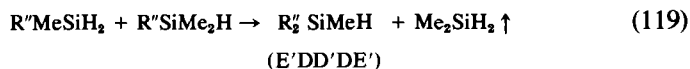
Products with four silicons are secondary products arising from further reactions of the first-turnover products, namely Eqs. (114) and (115), which represent SiO/Me and SiO/H exchange, respectively. Five-silicon compounds are third-turnover products, etc.

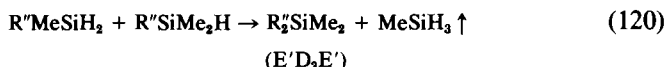


The products from the redistribution of E'DE' (Table IV) can be rationalized only in part by the types of exchanges seen so far. Writing E'DE' (HSiMe₂OSiMe₂OSiMe₂H) as R''SiMe₂H to highlight the exchange processes, we expect R''/Me, R''/H, and Me/H exchanges as shown in Eqs. (116–118) (R'' = HSiMe₂OSiMe₂O—). Dihydride **32** is expected to be



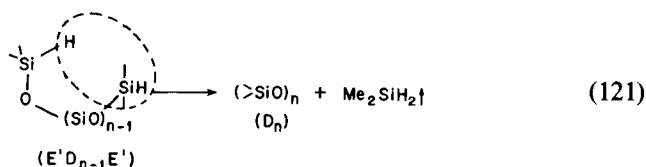
very reactive and rearrange according to Eqs. (119) or (120).



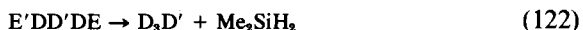


SiO/Me and SiO/H exchanges are usually the most facile, so that the products of these exchanges [Eqs. (116) and (117)] are expected to constitute the bulk of the first-turnover products. It is somewhat surprising therefore that the cyclic D₃D' and the four-silicon oligomer E'D₂E' constitute the bulk of the products.

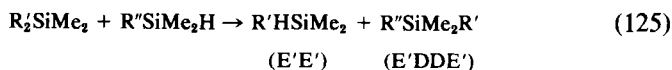
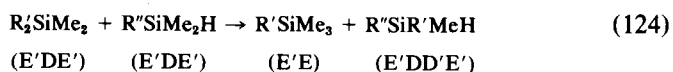
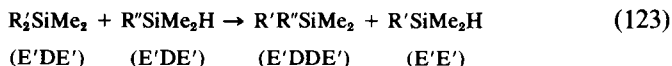
We have not as yet discussed the formation of the cyclics that are also observed in the E'E' disproportionation (Table II). There is as yet no experimental evidence for the mechanism of their formation, but it seems reasonable that the cyclics arise from an "internal" SiO/H redistribution, as shown in Eq. (121). If this is the case, then the oligomer E'DD'DE,



which is expected to be the major component, must rapidly cyclize according to Eq. (122), thus accounting for the D₃D' cyclic and the lower than expected amount of the five-silicon linear compound. It is puzzling, however, that the E'D₃E' does not give appreciable quantities of D₄, but the lack of D₄ with the Ir-based catalyst is consistent with the very low abundance of D₄ in the E'E' disproportionation (Table II).

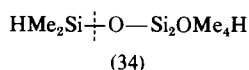
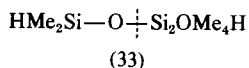


The other puzzling aspect of the product distribution in Table IV is the presence of large amounts of E'D₂E'. This is the product if the end siloxy group [(HSiMe₂O)—SiMe₂OSiMe₂H] in E'DE' is exchanged. Representing this end group as R', then the SiO/SiO, SiO/Me, and SiO/H exchanges shown in Eqs. (123–125) (R' = HSiMe₂OSiMe₂O—) are possible in principle.

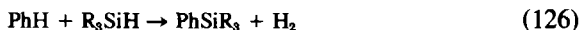


Because neither product of Eq. (124) is observed, we conclude the R'/Me

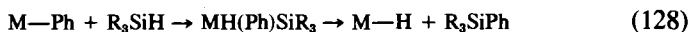
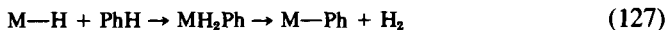
exchange does not occur. The E'E' produced in Eqs. (123) or (125) would rapidly react with the E'DE' (present in large excess) to give E'D₂E' and Me₂SiH₂ [Eq. (107)]. The odd thing about the exchanges in Eqs. (123) or (125) is that the Si—O bond β to the Si bearing the hydrogen is broken (33) rather than the more common α-scission mode (34).²



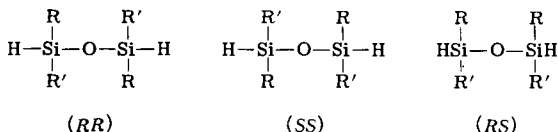
A rather interesting aspect of the products reported in Tables II and III is the appearance of phenylsiloxanes and phenylsilanes (68). There are only three possible sources of phenyl groups in these systems: (1) the benzene solvent, (2) the phenyl groups on the Ph₃P ligands of the catalyst, and (3) the chromatography column. By running these reactions in benzene-*d*₆, it was demonstrated that the solvent is the source of the phenyl groups when L₂Ir(CO)Cl is the catalyst precursor, but the Ph₃P groups are the source when L₃RhCl is the catalyst precursor. Thus, with the Ir catalyst the net reaction is as shown in Eq. (126) and represents the first for-



mation of phenyl silicon compounds from benzene and silicon hydrides mediated by metal complexes. A possible catalytic cycle is shown in Eqs. (127–128) where M = L₂Ir(CO). This reaction represents the first low-energy substitution of hydrogen on benzene by silicon and is only the second reported example of C—H activation for other than simple H/H or H/D exchange (69, 70).

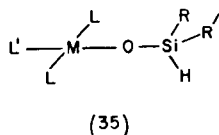


Symmetrically substituted disiloxanes of the type (HRR'Si)₂O have two optically active centers and thus exist as mixtures of *d*, *l* and meso isomers, denoted as (*RR*), (*SS*), and (*RS*), respectively. During the



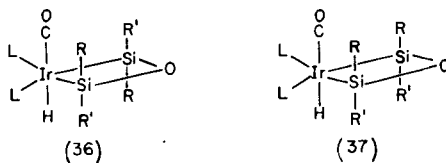
L₂Ir(CO)Cl-catalyzed oligomerization of tetraalkyldisiloxanes, intermediates (e.g. 35) are proposed. By virtue of the substitution on Si, this com-

² An alternative, and more likely, explanation for the appearance E'D₂E' is the comproportionation reaction between E'D₃E' (the principal first-turnover product) and the starting E'DE': E'D₃E' + E'DE' → 2E'D₂E'. This does not require β-scission.



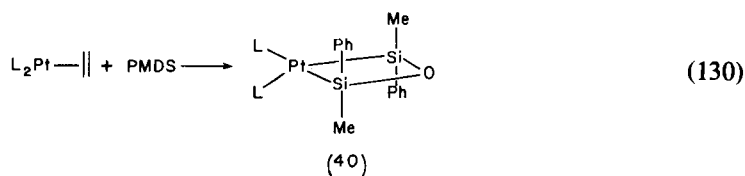
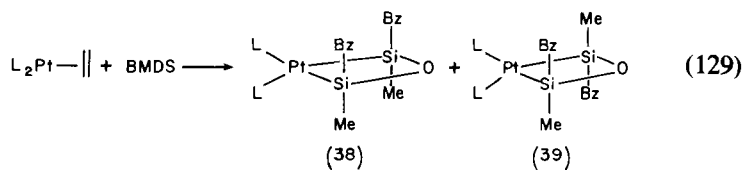
plex is optically active and might be expected to discriminate between the *d,l* and meso isomers of the tetraalkyldisiloxane during the oxidative addition step in the proposed oligomerization mechanism (see Step C of Scheme I). Such discrimination could lead to stereoregular growth of the oligomeric siloxanes, i.e., it is conceivable that the metal-catalyzed polymerization of tetraalkyldisiloxanes could lead to stereoregular silicones via asymmetric selectivity (71).

Furthermore, it is expected that two stereoisomers of the four-membered ring will differ in stability. If R' is a bulky group, the trans isomer



(36) is expected to be more stable than the cis isomer (37), thus giving selectivity in the formation of chiral catalyst (35).

We have been unable to isolate pure metallacycles of type 36 or 37 from the interaction of either (HPhMeSi)₂O (PMDS) or (HBzMeSi)₂O (BMDS) with Vaska's complex. White solids are obtained which show over ten Si—Me peaks in the NMR spectrum. However, both PMDS and BMDS react with (Ph₃P)₂Pt(C₂H₄) to form platinadisiloxanes [Eqs. (129) and (130)] (72). The benzylmethylmetallacycles are obtained as a mixture of



the *cis* and *trans* isomers, **38** and **39**. The metallacycle obtained from the phenylmethyldisiloxane (PMDS) gave only one isomer to which we assign the *trans* structure **40**. Apparently, the benzyl groups are capable of rotating into positions that decrease the steric repulsions to the point that no discrimination is made between the *d,l* or *meso* isomers. The phenyl groups are sufficiently bulky that the *d,l* pair, which gives the *trans* isomers **40**, reacts with $L_2Pt(C_2H_4)$ preferentially over the *meso* isomer.

If the metal-catalyzed reactions of PMDS or BMDS were to be strictly analogous to the oligomerization of tetramethyldisiloxane, we would expect the idealized reaction shown in Eqs. (131) or (132) to occur [cf. Eq. (106)].



The products actually observed are shown in Tables V and VI. In these reactions, the extremely volatile fractions (e.g., $MeSiH_3$ and Me_2SiH_2) were allowed to escape and the solutions to date have been analyzed only by GC/MS. Tables V and VI show only those products boiling between approximately 70°C and 280°C.

TABLE V
VOLATILE REDISTRIBUTION PRODUCTS OF
1,3-DIPHENYL-1,3-DIMETHYLDISILOXANE $[(HPhMeSi)_2O]$

Product ^a	% ^b	Product ^c	% ^b
Me_3SiH	tr		
$PhMeSiH_2$	tr	$PhMeSiH_2$	10.6
$PhMe_2SiH$	11.2	$PhMe_2SiH$	8.6
Ph_2MeSiH	30.3	Ph_2MeSiH	71
Ph_3SiH	tr		
$Ph-Ph$	5.6	$Ph-Ph$	2.5
$HPhMeSiOSiMe_2H$	6.1	$PhMe_2SiOSiMe_2H$	1.4
$HPhMeSiOSiMe_2Ph$	1.8		
$HPhMeSiOSiPh_2H$	tr		
$HPh_2SiOSiPhMe_2$	2.8		
$HPhMeSiOSiPhMeEt$	2.4 ^d		
$HPhMeSiSiPh_2Me$			
$PhMe_2SiSiHPhEt$	2.0		
$Ph_2MeSiSiPhMe_2$	5.7		
$(HPhMeSiO)_2SiPhMe$	2.8		

^a Catalyst: 4.8 mol% (acac)Rh(C_2H_4)₂/40°C/1 h.

^b Area %.

^c 0.5 M disiloxane, 1.8 mM $L_2Ir(CO)Cl$, 40°C/38 h.

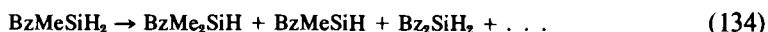
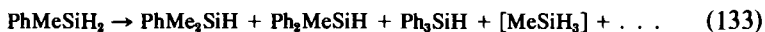
^d Incomplete GC separation, but mostly the disilane.

TABLE VI
VOLATILE REDISTRIBUTION PRODUCTS OF
1,3-DIBENZYL-1,3-DIMETHYLSILOXANE [(HBzMeSi)₂O]^a

Product	%	Product	%
BzMeSiH ₂	1.3	HBzMeSiOSiMe ₂ H	tr
BzMe ₂ SiH	63.1	Me ₂ HSiBzH ₂	12
Bz ₂ SiH ₂	1.6	MeBzHSiBzH ₂	14
Bz ₂ MeSiH	29	Bz—Bz	4

^a 0.5 M (HBzMeSi)₂O, 1.6 mM L₂Ir(CO)Cl in benzene, 40°C/45 h.

The monosilane fractions probably arise from the further disproportionation of the RMeSiH₂ (R = Ph or Bz) produced according to Eqs. (131) or (132) [compare the products in Table V and Eq. (34) ff.].



It is interesting to note that Ph₂MeSiH is the major monosilane from the disproportionation of PhMeSiH₂ but that BzMe₂SiH is the major monosilane from BzMeSiH₂. It therefore appears that phenyl migration is more facile than methyl migration, but methyl is more facile than benzyl migration in these disproportionations.

Products arising from the redistribution of groups on the starting disiloxanes are also produced, along with sizable fractions of disilanes. With (acac)Rh(C₂H₄)₂ as catalyst precursor, products from the hydrosilation of the coordinated ethylene are also detected. Only a low yield is obtained of the trisiloxane (HPhMeSiO)₂SiPhMe, the first member of the oligomeric family predicted by Eq. (131). Due to the method of analysis, the higher boiling members of this series would not be detected. However, from a mass balance, it is obvious that the siloxane fraction is either extensively cross-linked with Si—Si bonds or is rich in hydrogen [the mole ratio of the groups unaccounted for in the mass balance of the L₂Ir(CO)Cl-catalyzed reaction is Ph_{0.3}MeHSiO]. It thus appears that with PMDS or BMDS, the rate of ligand redistribution is competitive with the rate of oligomerization, thus dooming any hopes of obtaining stereoregular silicones with the present catalyst systems.

With one exception (the Me/Cl exchange in Table I), all redistributions of siloxanes catalyzed by transition metals observed to date occur only when at least one silicon-hydrogen bond is present in the molecule. We have established that hexamethyldisiloxane (EE) and hexamethylcyclotrisiloxane (D₃) are completely inert under the same conditions that cause extensive redistribution of hydridosiloxanes.

It is probable that other groups (e.g., vinyl, ethynyl) that interact strongly with low-valent metal centers would also "activate" the siloxanes toward redistribution, although these have not yet been investigated.

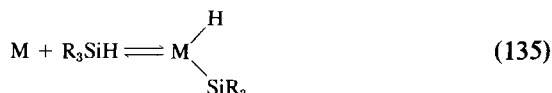
It is apparent from the examples in this section that the lability of the groups on silicon is greatly dependent on the catalyst. With conventional acid or base catalysts, SiO— is classed as a "labile" ligand, SiH as "semi-labile," and Si—R (R = alkyl or aryl) as "nonlabile" (1). However, with low-valent complexes of the group VIII metals, SiH is the most labile ligand, and SiO— and Si—R appear to have comparable reactivities. Hence, these two sets of catalysts types are complementary in their capacity to redistribute ligands on silicon.

III

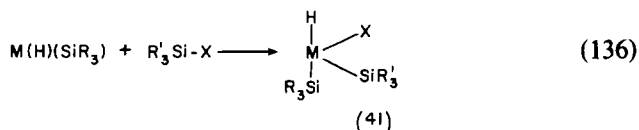
MECHANISTIC CONSIDERATIONS

In spite of the many known silicon-transition metal complexes (15, 16), little systematic work has appeared on the reaction mechanisms of silyl metal complexes. This state of affairs is in marked contrast to the current work on σ -alkyl transition metal complexes, where much emphasis is placed on determining detailed "decomposition" mechanisms (73-76). The reason for the interest in decomposition mechanisms is that the products of a transition metal-catalyzed reaction are released by the decomposition of the product-metal complex. Thus, to understand a catalytic process, one must have knowledge not only of the interaction of the reactants with the metal (leading to a substrate-metal complex), but also of the mechanisms whereby substrates are transformed on the metal and the manner in which the products are released.

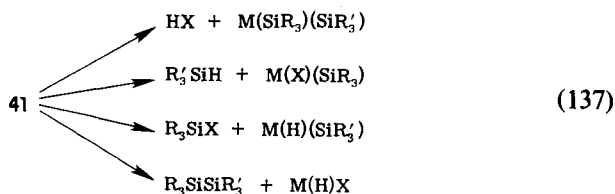
Consider, for example, the interaction of a silyl hydride R_3SiH with a zero-valent metal species M [M could be $L_2Pt(0)$]. An oxidative addition gives a silyl metal hydride [Eq. (135)] (77). A simple series of oxidative



additions and reductive eliminations in which the metal oscillates between the oxidation of zero and two cannot exchange ligands on Si. A further oxidative addition in which the metal goes to the formal IV oxidation state is required [Eq. (136)]. Depending on the groups R, R', or X, as well as

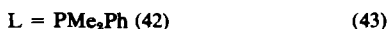


the ancillary ligands on M, complex **41** can "decompose" by four distinct paths [not counting the reverse of Eq. (136)].



The metal species in Eq. (137) can react further by reductive eliminations or oxidative additions to give, ultimately, the spectrum of products often observed in the redistribution reaction. The actual product distribution thus depends not only on the relative rates at which the substrates react with the metal center, but also on the relative rates of the reductive elimination steps in Eq. (137). It is worth noting that differences in activation energies of two parallel reactions of only a few kcal/mol can lead to a 100-fold difference in their rates. Hence, seemingly slight changes in ligands on the metal or groups on the silicon can drastically alter the product distribution in a quite unpredictable manner.

For example, complex **42** reacts with HCl to give the silyl hydride and **44** via the Pt(IV) complex **43** (78).



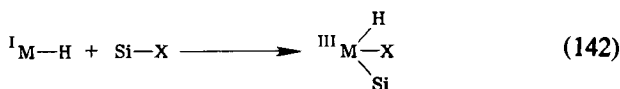
Complex **44** reacts with HCl to eliminate the silyl *chloride*.



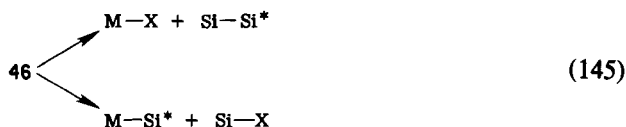
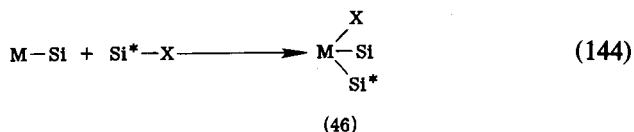
In contrast, changing the phosphine ligand to "diphos" ($Ph_2PCH_2CH_2PPh_2$) gives *two* moles of silyl hydride upon reaction with 2HCl [Eq.



(141)]. The complex $L_2Pt(H)_2(Cl)(SiPh_2Me)$ ($L = PhMe_2P$) also eliminates the silyl hydride (79).

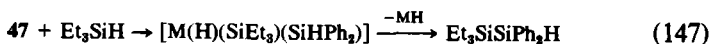
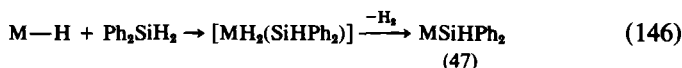


(45) ($\text{M} = \text{L}_2\text{Ir}$ or Rh)



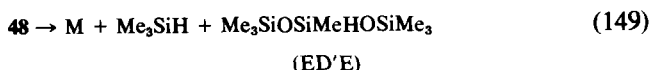
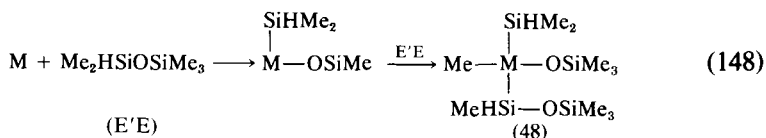
Metals (e.g., Ir and Rh) with stable +1 and +3 oxidation states can redistribute ligands on silicon by a series of oxidative additions and reductive eliminations [Eqs. (142–145)]. Each $\text{M}(\text{III}) \rightarrow \text{M}(\text{I})$ reductive elimination generates anew a $\text{Rh}(\text{I})$ or $\text{Ir}(\text{I})$ species which inserts into a SiX linkage. Normally $\text{X} = \text{H}$, but an occasional insertion into $\text{Si}-\text{C}$ or $\text{Si}-\text{O}$ bonds would lead to the observed redistributions.

Some of these catalytic cycles lead to products that appear to arise from divalent silylenoid species. However, most of the products that are put forward as evidence of silylenoid species can be formed straightforwardly by simple addition/elimination cycles. Such is the case with the oligomerization of disilanes and the disproportionation of silanes (e.g., R_2SiH_2). For example, $\text{Et}_3\text{SiSiPh}_2\text{H}$ is an expected product of the reaction of Et_3SiH and Ph_2SiH_2 via an addition/elimination scheme [cf. Eq. (39)].

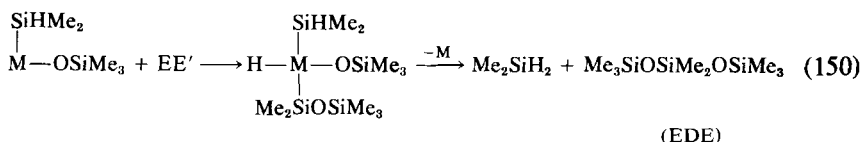


Although it appears that a Ph_2Si species has “inserted” into the $\text{Si}-\text{H}$ bond of Et_3SiH , no such divalent species need be postulated.

Even though much of the purported evidence for silylenoid species is weak or nonexistent upon close examination, such species may nevertheless be produced, especially if the possibility of dinuclear complexes is considered. In fact, there are several lines of evidence which do suggest that some sort of silylenoid species is generated from silanes and low-valent metal complexes. First, as Eq. (74) implies, the same dimethylsilicon metal complex is apparently generated from two diverse silicon compounds. Second, even early in the reaction, the most abundant product in the disproportionation of EE' is $ED'E$, which is the result of a SiO/Me exchange. If the redistribution were occurring solely by addition/elimination [e.g. Eqs. (142–145)], then the observed SiO/Me exchange is the result of insertion into Si—O and Si—C bonds [Eqs. (148–149)]. Now,



there is no question but that insertion into Si—H is the most facile of the possible insertions into the bonds of EE' . Hence, even if on occasion the metal inserts into an Si—O bond, for example, the next insertion would surely be into the Si—H bond [Eq. (150)].



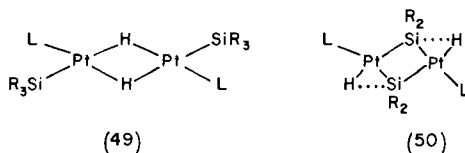
In other words, a SiO/Me exchange is the result of compounding two improbable insertions, so that simple addition/elimination mechanisms predict SiO/H or Me/H to be the more common exchanges (other than the degenerate H/H exchange). Since this prediction is contrary to fact, some other mechanism must be responsible for SiO/Me exchanges.

A major problem in postulating silylenoid metal complexes as intermediates in the redistribution reactions is simply that good model compounds are lacking, and the decomposition mechanisms of silyl transition metal complexes have not been systematically investigated. While there is evidence for transient $R_2\text{Si}$ species produced by thermal or photochemical means (80–83), there are no known monomeric silylene metal complexes. Several monomeric stannylene and germylene complexes are

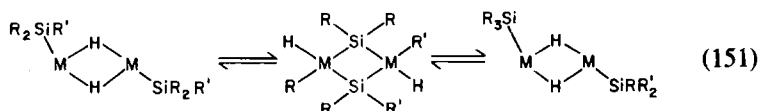
known however, reflecting the greater stability of the +2 oxidation state of the heavier group IV congeners (84–87).

The known silylene metal complexes are all dimeric, with R_2Si groups bridging two metals. However, dinuclear complexes appear not to have been considered as catalysts for redistribution reactions or even hydrosilations. Haszeldine *et al.* (88) found that the relative rates of isomerization and hydrosilation depended on the catalyst concentration, with the ratio, $k(\text{isom})/k(\text{hydrosil})$, decreasing with decreasing catalyst concentration. Such a dependence can occur only if the order of the two reactions with respect to catalyst is different. A monomer–dimer equilibrium $2M \rightleftharpoons M_2$, with the monomer catalyzing hydrosilation and the dimer catalyzing isomerization would give $k(\text{hydrosil}) \propto [M]$ and $k(\text{isom}) \propto [M]^2$. Decreasing the concentration of catalyst would shift equilibrium to the monomer, thus increasing the relative rate of hydrosilation at the expense of isomerization.

Recently, a new class of platinum silyl complexes was reported (89–91). The complexes of type **49**, formed from $LPt(C_2H_4)_2$ (L = bulky phosphine) and trialkylsilanes, are extremely efficient hydrosilation catalysts. Upon heating, **49** is converted into **50** via an ill-defined α -elimination process. In all examples of redistributions, the presence of at least one hydro-



gen on silicon activates the silicon moiety toward redistribution. This effect might be steric in nature (i.e., the Si—C bonds are less shielded in a hydrosilane), but it may be that the activating influence of hydrogen results from the fact that the SiH group allows a ready attachment of the silyl group to the metal. Following the initial attachment, α -elimination in a dinuclear complex could lead to scrambling of the ligands [Eq. (151)].



At the present time, there is no strong experimental justification for any of the mechanisms mentioned in this chapter. It may be that a variety of mechanisms are operative, depending on the substrate and catalyst. Nevertheless, these speculations are put forth with the hope that they will stimulate new interest and research in this area.

IV

CONCLUSIONS

The transition metal-catalyzed redistribution of groups on silicon is relatively unexplored. Since the lability of groups toward migration is considerably altered vis-à-vis "conventional" catalysts, there is the strong possibility that the metal-catalyzed reactions could be useful in industrial conversions. Much work remains to be done in establishing the synthetic utility, especially with regard to the control of the selectivity of the reaction. In this regard, the selectivity of the "Benkeser" reaction [Eq. (46)] is remarkable. A complete understanding of the redistribution reaction, and even the *detailed* understanding of hydrosilation, must await further work on the mechanisms of decomposition of silyl metal complexes, especially of those complexes with both σ -alkyl and silyl ligands. Even without a good understanding of the mechanism, it is anticipated that the metal-catalyzed redistribution of groups on silicon will find increased use as a new synthetic tool of the organosilicon chemist.

ACKNOWLEDGMENTS

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The Application of ^{13}C -NMR Spectroscopy to Organo-Transition Metal Complexes

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I

INTRODUCTION

This review is based largely on investigations carried out in the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr. In view of the rapid expansion of ^{13}C -NMR spectroscopy and because of the limited space available here, we have made no attempt to give a comprehensive account of the applications of ^{13}C -NMR spectroscopy to organometallic chemistry and have intentionally restricted ourselves to those classes of compounds that are of particular significance to the research in this institute. Emphasis has been given to examples that illustrate the advantages of ^{13}C NMR in the routine investigation of organometallic complexes, and the reader is referred to a number of reviews for a more complete treatment of various organometallic aspects (1-4).

Because of the low intrinsic sensitivity of the ^{13}C nucleus (1.6% of that of the proton) and its low natural abundance (1.1%), the development of

Fourier transform techniques was necessary before routine measurement became possible. Indeed, the growth of the use of ^{13}C NMR in organometallic chemistry has followed closely the increase in sensitivity and flexibility of the instruments available.

Although in many cases the ^{13}C -NMR spectrum provides information similar to that obtainable from PMR, a number of potential advantages are obvious:

1. The carbon skeleton, including those atoms bonded to the metal, may be observed directly.

2. Organic ligands in which no protons are attached to the carbon atoms interacting with the metal may be investigated, e.g., π -bonded alkynes or substituted olefins, complexes formed by carbon monoxide or substituted carbenes.

3. The signal dispersion is much greater than that observed in PMR spectroscopy. This, combined with the fact that the signals in the proton-decoupled spectra are usually sharp singlets, is invaluable for the detailed analysis of complex systems, of mixtures or for detecting subtle structural differences (see, e.g., Section V).

4. Information on the hybridization of the carbon atom can be obtained from the $^1J(\text{CH})$ coupling constant.

5. Much faster exchange processes can be observed with ^{13}C NMR than with PMR (5). This is a consequence of the wider range of the chemical shifts in the former case which corresponds to approximately five times the frequency separation at a given field strength.

The sensitivity problem is, however, a handicap in the study of organometallic compounds, since these are frequently relatively insoluble. Increasing the sensitivity of the spectrometers will not only allow less-soluble compounds to be investigated, but will also allow more detailed examination of those for which simple proton-decoupled spectra can be measured.

Factors which increase the sensitivity include the following:

1. Increasing the sample size. Sample tube diameters of 10 and 12 mm have become standard, but wide-bore spectrometers which take up to 20-mm sample tubes are available. The necessarily large quantity of sample as well as of deuterated solvents, however, restricts their use in routine measurements.

2. Isotopic enrichment of the sample. This is practical only in selected cases.

3. Increasing the magnetic field strength. Until a few years ago most ^{13}C -NMR measurements were carried out using spectrometers having

field strengths of 1.9–2.4 T (corresponding to 20–25 MHz for ^{13}C and 80–100 MHz for ^1H); however, spectrometers equipped with superconducting magnets and having field strengths of 3.5–11.7 T (30–126 MHz for ^{13}C and 150–500 MHz for ^1H) have become commercially available. The advantages and disadvantages associated with ^{13}C NMR at high magnetic fields have been reviewed by Anet (6). Decoupled spectra are in general well resolved, so that in most cases a higher field offers relatively little advantage. Sensitivity should be increased, but for large molecules the enhancement due to the nuclear Overhauser effect (NOE) becomes frequency-dependent and may be considerably reduced and part of the higher intrinsic sensitivity of the spectrometer may be lost. The overall situation is more complicated if internal motion within the molecule occurs, and practice will have to show which combination of field strength and bore size gives the best results. Our initial experience with a 101-MHz spectrometer has indicated that a considerable gain in sensitivity over electromagnetic systems is to be expected.

The following aspects of high field measurements can be as important as increases in sensitivity.

1. ^{13}C -NMR spectra recorded, without proton decoupling, consist of well-separated multiplets at high fields, whereas at low field (measuring frequency 25 MHz or less) confusing overlap of the multiplets frequently occurs.

2. Since the NMR resonances of chemically different protons are more widely separated at higher field, ^{13}C -NMR spectra measured without proton decoupling will have more clearly defined multiplets, and as a result the magnitudes of proton–carbon coupling constants will be more easily extracted. A good illustration of this aspect is the proton-coupled spectra of propene recorded at 25 and 101 MHz discussed by Dubs and von Philipsborn (7).

3. The temperature range over which accurate kinetics can be measured is greater at higher field. For example, for a simple two-site exchange with equal populations in each site, the broadening in the region of fast chemical exchange varies as the square of the magnetic field. The coalescence temperature is proportional to the frequency difference of the exchanging species and therefore coalescence is reached at a higher temperature.

A brief discussion of the various NMR parameters follows. The reader is referred to Stothers and other authors (8–12) for a detailed treatment of theoretical aspects. All chemical shifts listed in this review are given in the δ scale relative to TMS (positive to lower field).

A. The Coordination Chemical Shift

Complexation of an organic ligand to a metal is invariably accompanied by changes in the chemical shifts of the ligand carbon atoms. These effects are conveniently analyzed in terms of the coordination chemical shift which, for the n th nucleus of a ligand, is defined as

$$\Delta\delta n = \delta n_{\text{complex}} - \delta n_{\text{ligand}}$$

The typical olefinic carbon coordination shift to higher field is therefore negative. In the case of the η^1 -alkyl metal complexes (M-R) it is useful to compare the shifts with those of the corresponding hydrocarbon (H-R).

Empirical additivity relationships have proved invaluable for assigning the ^{13}C signals of organic compounds (10). Corresponding data for organo-transition metal compounds are limited, but this approach may be expected to become of increasing importance and is emphasized here.

B. Coupling Constants

Spin-spin coupling constants involving ^{13}C nuclei are usually dominated by the Fermi contact term (12) and therefore depend in part upon the hybridization of the interacting nuclei. The ^{13}C - ^1H coupling constants, $J(\text{CH})$, are a useful indication of the hybridization of a given carbon atom. Typical ranges for hydrocarbons are approximately 125 Hz for sp^3 carbon atoms in alkanes, 155–160 Hz for sp^2 carbon atoms in alkenes and arenes, and approximately 250 Hz for alkynes (8). Applications to structural determinations are mentioned throughout this review.

The magnitudes of the coupling constants, as well as the number of protons directly attached to the carbon atoms, can be obtained by measuring gated decoupled spectra in which proton-coupled spectra are recorded with retention of the NOE (13). These spectra, however, have relatively low signal-to-noise ratios. An alternative approach which also permits the multiplicities to be obtained is to measure single-frequency off-resonance decoupled spectra; but while these have a relatively good signal-to-noise ratio, they cannot be used to determine the magnitude of the coupling directly.

C. Integration

Under normal measurement conditions with broad-band proton decoupling and short measurement cycles (pulse repetition rates typically of the order of 1 sec), ^{13}C signals cannot be integrated because of the widely dif-

fering relaxation times (T_1) and variations in the magnitude of the nuclear Overhauser enhancement from carbon to carbon. More reliable integrals may be obtained by introducing paramagnetic reagents such as $\text{Cr}(\text{acac})_3$ (14) to reduce the relaxation times and quench NOE effects or from a gated decoupled spectrum in which the NOE is eliminated while decoupling the protons (13) and for which the pulse separation is at least $4-5 T_1$ (14). As far as organometallic complexes are concerned, the addition of relaxation reagents may be chemically undesirable while the gated method is seldom practical because of the greatly reduced signal-to-noise ratio that can be achieved within a reasonable measurement time. However, reliable estimates of the relative concentration of isomeric complex species can be obtained under standard measurement conditions by comparing absorptions that are chemically and spectroscopically related, since the correlation times and relative contributions of the various relaxation mechanisms will in these cases be virtually identical. For example, accurate values for the relative proportions of the four isomers present in solutions of bis(η^3 -1,3-dimethylallyl)nickel can be obtained by comparing the intensities, in the ^{13}C -NMR spectrum of the two methyl signals, of the terminal allyl carbon signals or of the meso carbon signals (see Fig. 8).

D. Relaxation Times

Although ^{13}C -NMR relaxation times have been frequently used in studying the structures and dynamics of organic and main-group organometallic compounds (15-17), the extension to organo-transition metal compounds has seldom been made. Among the earliest compounds to be studied was the substituted ferrocene derivative (1) and from the relaxation data it was shown that the rate of rotation of the unsubstituted ring is seven times faster than that of the saturated ring (18). Recently, the relaxation mechanisms of enriched transition metal-methyl compounds have been investigated, and it was shown that in general C-H dipolar and internal spin rotation mechanisms are operative; a methyl rotation barrier of 0.8(4) kcal/mol was found, for example, for **2** (19).

Selected spin-lattice relaxation times are shown in Fig. 1. Carbon nuclei bonded to protons in typical complexes of the type reviewed here frequently have short spin-lattice relaxation times (T_1) and hence relatively large tilt angles can be used in routine FT measurements. T_1 is considerably longer for carbon nuclei not directly bonded to protons, e.g., a value of 56 sec has been measured for the meso-allyl carbon atom in **6**, which accounts, in part, for the low intensity of the signals of such nuclei under "standard" measurement conditions.

For relatively large complexes, such as those containing two or more

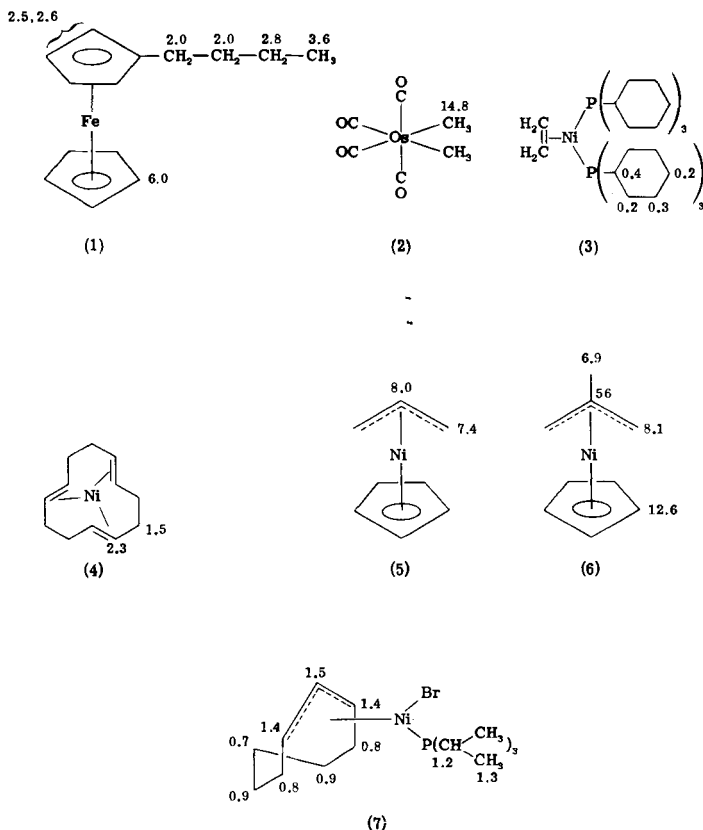


FIG. 1. Typical ^{13}C spin-lattice relaxation times (T_1 in seconds) for organo-transition metal complexes. (1) Benzene- d_6 , 38°C (18); (2) benzene- d_6 , 38°C (19); (3) benzene- d_6 , 35°C; (4) toluene- d_8 , 0°C; (5), (6), and (7) toluene- d_8 , 35°C. All measurements at 25.2 MHz.

tricyclohexylphosphine ligands, the increase in the correlation time is reflected in the decrease in the relaxation time (3). While this does not normally present difficulties at ambient temperature, viscosity broadening can become problematic even at moderately low temperatures.

Figure 2 shows the results of a T_1 determination for $(\eta^3\text{-cyclo-C}_8\text{H}_{13})\text{-Ni}(\text{Br})\text{P}[\text{CH}(\text{CH}_3)_2]_3$ (7) using the inversion recovery method. All carbon atoms in this compound are directly bonded to at least one proton, and T_1 lies in the range 0.7–1.5 sec, whereby the relaxation times within the cyclooctenyl ring are approximately proportional to the number of associated protons: a result expected for predominantly dipole–dipole relaxation.

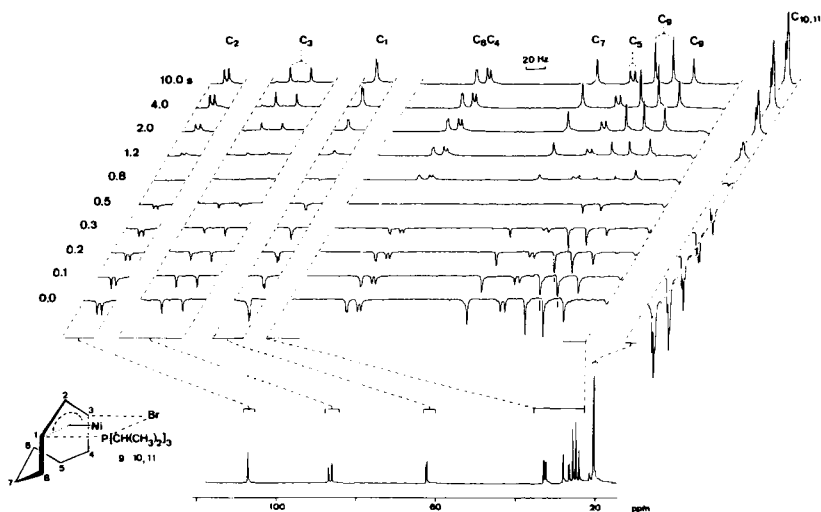


FIG. 2. Determination of the relaxation times of $(\eta^3\text{-cyclo-C}_8\text{H}_{18})\text{Ni}(\text{Br})\text{P}[\text{CH}(\text{CH}_3)_2]_3$ (7) by the inversion recovery technique (toluene- d_8 , 35°C , 25.2 MHz). The spectra have been stacked as a function of the time interval between the 180° and 90° pulses.

II

η^1 -ALKYL COMPLEXES

Data for some typical η^1 -alkyl derivatives are collected in Table I (8, 20–23). The chemical shifts are analyzed conveniently in terms of the substituent effects relative to the corresponding parent hydrocarbon (10). The chemical shifts of carbon atoms directly attached to a metal (C_α) are strongly dependent on both the metal and the nature of the ligands present, and shifts to both higher and lower field relative to the parent hydrocarbon have been observed. Unexpectedly low shielding is found in some complexes of Ta, Nb, Hf, and Zr (see Table I). The carbon atom β to the metal generally experiences a small and relatively constant shift to lower field, while the γ -carbon atom is either practically unchanged or is shifted slightly to lower field. In this last case, the effect of the metal contrasts with that of most other substituents.

Representative $^1J(\text{CH})$ coupling constants are shown in Fig. 3. (20, 23–25) As should be expected for an sp^3 carbon bonded to an electropositive atom, the coupling constant $^1J(\text{CH})$ for C_α is often somewhat reduced from the typical value of 125 Hz found in hydrocarbons. There are, however, exceptions and examples are shown (Fig. 3) in which values greater

TABLE I
¹³C-NMR DATA FOR SELECTED METAL-ALKYL COMPOUNDS

Compound	Temperature (°C)	Solvent	δC _α	ΔδC _α ^a	δC _β	ΔδC _β ^a	J(PC _α)
CH ₃ Ni(acac)P(CH ₃)	-30	Toluene- <i>d</i> ₈	-10.2	-8.1			44.1
CH ₃ Ni(acac)P(C ₆ H ₁₁) ₃	35	Toluene- <i>d</i> ₈	-13.8	-11.7			40.5
CH ₃ CH ₂ Ni(acac)P(C ₆ H ₁₁) ₃	35	Toluene- <i>d</i> ₈	-1.5	-7.4	15.2	9.3	35.6
CH ₃ CH ₂ CH ₂ Ni(acac)P(C ₆ H ₁₁) ₃ ^b	35	Toluene- <i>d</i> ₈	8.9	-6.7	23.9	7.8	35.0
CH ₃ CH ₂ Ni(acac)P(C ₆ H ₅) ₃ ^c	25	Toluene- <i>d</i> ₈	6.8	0.9	13.9	8.0	—
(CH ₃ CH ₂) ₂ Nibipy ^d	68	Benzene- <i>d</i> ₆	10.6	-4.7	16.0	11.1	—
(CH ₃) ₂ Ta(benzynes)-η ⁵ -C ₅ (CH ₃) ₅ ^e	—	Benzene- <i>d</i> ₆	52.7	54.8			—
(CH ₃) ₂ Nb(benzynes)-η ⁵ -C ₅ (CH ₃) ₅ ^e	—	Benzene- <i>d</i> ₆	44	46			—
CH ₃ CH ₂ Nb(C ₂ H ₄)(η ⁵ -C ₅ H ₅) ₂ ^f	35	Benzene- <i>d</i> ₆	11.2	5.3	20.3	14.4	—

^a Relative to the free hydrocarbon; see Stothers (8). ^b J(PC_γ) = 3.8 Hz; δC_γ 17.5; ΔδC_γ +1.9. ^c Cotton *et al.* (20). ^d Yamamoto *et al.* (21).
^e McLain *et al.* (22). ^f Klazinga and Teuben (23).

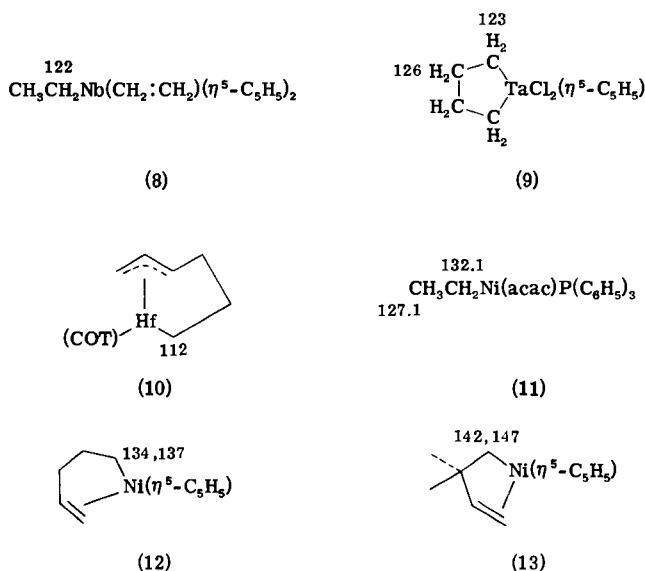


FIG. 3. $^1J(\text{CH})$ (Hz) for representative metal-alkyl compounds: **8**, Klazinga and Teuben; (23); **9**, McLain *et al.* (24); **11**, Cotton *et al.* (20); **12** and **13**, Lehmkuhl *et al.* (25).

than 130 Hz have been observed. The influence of bond angles on the coupling constant is convincingly demonstrated by the chelating η^1, η^2 -alkenyl complexes **12** and **13**: the already relatively high value of 134–137 Hz for the methylene carbon atom α to nickel in the 4-alkenyl complexes increases to 142 and 147 Hz on going to the 3-alkenyl complex (this molecule is chiral). This is clearly a result of rehybridization of the α -carbon atoms toward sp^2 on forming the more strained system. At the same time, the C_α resonance is shifted more strongly upfield [$\Delta\delta$ is approximately -7 ppm for **12** (compared to 1-pentene) and -37 for **13** (compared to 3,3-dimethylbutene)].

A bridging methyl group may also show a large shift to high field. In the case of the $(\eta^3\text{-1,3-dimethylallyl})\text{nickel}$ methyl dimer (**14**), the structure of which has been confirmed by X-ray crystallography (26), the bridging methyl groups resonate at -20.3 ppm [$^1J(\text{CH}) = 118$ Hz].

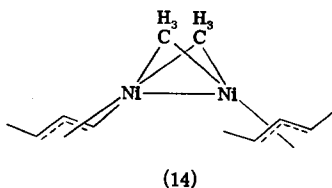
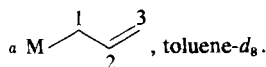


TABLE II
¹³C-NMR CHEMICAL SHIFTS FOR SELECTED η^1 -ALLYL-METAL COMPLEXES

Complex	Temperature (°C)	δC_1^a	δC_2	δC_3	Reference
$CH_2:CHCH_2W(CO)_3\eta^5-C_5H_5$	—	-6.6 ^b	146.0	107.3	28
$CH_2:CHCH_2Ru[P(C_6H_5)_3]_2\eta^5-C_5H_5$	+35	3.7	154.4	99.9	29
$CH_2:CHCH_2Pd[P(CH_3)_3]\eta^3-C_3H_5$	-90	16.8	148.1	100.0	30
$CH_2:CHCH_2Pt[P(CH_3)_3]\eta^3-C_3H_5^c$	-50	12.4	149.0	102.6	30
$(CH_2:CHCH_2)_2Zn^d$	-100	20.0	145.4	99.8	31
$(CH_2:CHCH_2)_4Sn^e$	R.T.	16.2	136.3	112.2	32



^b ¹J(WC) 29.5 Hz.

^c J(PC₁) 5.3, J(PC₂) 3.3, ¹J(PtC₁) 770.3, ²J(PtC₂) 73.3, ³J(PtC₃) 69.6 Hz.

^d THF-*d*₈/ether-*d*₁₀: at 38°C exchange; $\delta(C_1 + C_3) = 61.4$, $\delta C_2 = 143.7$.

^e Neat liquid.

In general, the methylene group in allyl derivatives of the type $X-C^1H_2-C^2H=C^3H_2$ tends to "insulate" the terminal carbon atom (C_3), and to a lesser extent the central carbon atom (C_2) from polar substituents (27). As a result, the chemical shifts of a wide variety of compounds where X is alkyl, Hal, OR, NR₂, SiX₃, SnX₃, PX_n, etc. fall within a relatively narrow range: $\delta C_3 = 116 \pm 3$ ppm and $\delta C_2 = 135.5 \pm 4$ ppm. However, the chemical shifts for the corresponding η^1 -allyl-transition

 TABLE III
¹³C-NMR DATA FOR η^1 -ALLYL- $Ru[P(C_6H_5)_3]_2(\eta^5-C_5H_5)$ COMPLEXES^a

η^1 -Allyl group	δC_1	$\Delta\delta C_1^b$	δC_2	$\Delta\delta C_2^b$	δC_3	$\Delta\delta C_3^b$	δC_5H_5	δCH_3
$Ru \begin{array}{c} 1 \\ \\ C=C \\ \\ 2 \end{array} \begin{array}{c} 3 \end{array}$	3.7	-15.7	154.5	20.9	99.9	-16.1	85.6	—
$Ru \begin{array}{c} \diagup \\ C=C \\ \end{array}$	6.9	-17.3	nd		101.6	-9.7	84.2	26.5
$Ru \begin{array}{c} \diagup \\ C=C \\ \diagdown \end{array}$	1.5	-15.3	148.1	22.7	110.4	-15.0	85.4	18.4
$Ru \begin{array}{c} \diagup \\ C=C \\ \diagdown \end{array}$	-3.6	-15.0	147.1	22.9	109.1	-15.1	84.8	13.9
$Ru \begin{array}{c} \diagup \\ C=C \\ \end{array}$	-3.1	-16.4	142.3	23.6	115.8	-15.9	84.6	26.3, 18.6

^a Benzene-*d*₆ or toluene-*d*₈, 35°C (29).

^b $\delta(RH)$; see de Haan *et al.* (33).

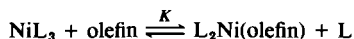
metal complexes are found at some 10 ppm to higher field (C_3) and 15 ppm to lower field (C_2), respectively, suggesting that here the metal is interacting in some way with the double bond (a direct π -interaction is ruled out by the direction of the shift of the central carbon atom). As expected, the chemical shift of the methylene carbon atom (C_1) is dependent on the nature of the metal and associated ligands (Table II) (28–32). The ^{13}C -NMR data for a number of η^1 -allyl-transition metal complexes are shown in Table II. Within a given series the chemical shifts of the η^1 -allyl metal complexes show regular substituent effects relative to the corresponding olefin, and this is illustrated in Table III (29, 33) for a series of η^1 -allyl- $\text{Ru}[\text{P}(\text{C}_6\text{H}_5)_3]_2$ - η^5 - C_5H_5 complexes.

III

OLEFIN COMPLEXES

Complexation of olefins to transition metals is generally accompanied by a large shift of the olefinic carbon resonances to higher field. The origin of this effect is still the subject of considerable speculation (34–41), but a conventional interpretation based upon the Dewar–Chatt–Duncanson model of the bonding in metal–olefin complexes has proved useful (34). In this interpretation the interaction between the metal and π -electrons of the olefin is suggested (1) to reduce the electron density at the olefinic carbon atoms and (2) to reduce the carbon–carbon bond order and thus the π character of the olefin; the metal–olefin π^* -interaction is suggested (3) to increase the total electron density and (4) to reduce the π character of the olefinic carbon atom. Of these effects, only the first should decrease the shielding of the olefinic carbon atoms, while the remainder should cause an increase. However, the theoretical basis of this approach, as well as the suggestion that the shift changes are due to alterations in the nonbonded shielding term associated with partially filled d orbitals, (37, 38), has been criticized (39).

In spite of the lack of consensus concerning the interpretation, there is a mass of empirical data which indicate that $\Delta\delta$ correlates with the strength of the metal–olefin π^* -interaction. For example, Tolman *et al.* have shown for a series of $[(\text{CH}_3\text{-}o\text{-}\text{C}_6\text{H}_4\text{O})_3\text{P}]_2\text{Ni}(\text{olefin})$ complexes (olefin = $\text{CH}_2\text{:CH}_2$, CH:CHCN , maleic anhydride, etc.) that $\Delta\delta$ correlates with the equilibrium constant K for the reaction



This relationship between K and π^* -interaction is supported by the electronic and ESCA spectra of these complexes (41). A rough correlation has also been shown to exist between the $\Delta\delta$ values for a series of ethylene complexes and both the C=C stretching frequency and the C=C bond length (41, 42). In addition, several groups have shown that the upfield shift of the olefinic carbon atoms in phosphine complexes correlates with the basicity of the phosphine (*vide infra*).

It should, however, be stressed that a variety of other factors have an influence upon the complexation shift. These include changes in delocalization (this may be expected to be particularly important for olefins having electron-withdrawing substituents) and changes in conformation (this may well be of importance for systems involving butadiene and related compounds and chelating olefins).

In contrast to the chemical shift, the values for $^1J(\text{CH})$ alter little upon complexation. It has, however, been pointed out (41) that since the coupling in free ethylene (157 Hz) and in cyclopropane (161 Hz) is very similar, it is to be expected that this coupling will be relatively insensitive to any contribution from a metallacyclopropane form and hence provide little insight into the nature of the metal-carbon bond.

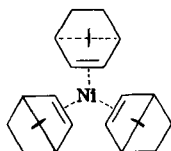
We have chosen to limit our contribution to a discussion of trigonal and tetrahedral zerovalent metal complexes and to butadiene-metal complexes.

A. Trigonal Planar Complexes

Data for a series of trigonal planar metal-olefin complexes are brought together in Table IV. Calculations made by Rösch and Hoffmann (43) suggest that a trigonal planar arrangement of the olefin molecules about the central metal atom is energetically preferred, and this has been confirmed crystallographically for a number of cases (see, e.g., 44, 44a).

The olefin signal in the tris(ethylene)metal complexes experiences a coordination shift of approximately -60 ppm. Interestingly, the magnitude of the complexation shifts increases in the order $\text{Pd} < \text{Ni} < \text{Pt}$. This result has also been observed for the bis(η^3 -allyl)metal complexes discussed in Section IV.

The simple four-line spectrum observed for tris(bicycloheptene)nickel at room temperature indicates that rapid rotation about the nickel-olefin axis is occurring: on reducing the temperature to -60°C , the spectrum consists of the 11 signals expected for conformation 15, which is also that observed in the crystal (44, 45).



(15)

Similar effects have been observed on cooling solutions of bis(bicycloheptene) NiL and bis(ethylene) ML ($\text{M} = \text{Ni}, \text{Pt}$) complexes (see Table IV). For example, the spectrum of $(\text{CH}_2:\text{CH}_2)_2\text{PtP}(\text{CH}_3)_3$ which consists of a single triplet at room temperature [$\delta 35.7$, $J(\text{PtC})$ 146 Hz] gives two signals at -50°C at 37.9 [$J(\text{PtC})$ 139; $J(\text{PC}) -7$ Hz] and 33.0 [$J(\text{PtC})$ 158; $J(\text{PC})$ 16 Hz], that with the largest P—C coupling being assigned to the carbon atom more trans to the phosphine (46).

One of the smallest coordination chemical shifts for zerovalent nickel-olefin complexes is observed for (*t,t,t*-CDT) Ni ($\Delta\delta = -25.0$ ppm). This is undoubtedly a result of the unfavorable propeller-like arrangement of the double bonds about the nickel atom. A considerably larger value of -40.5 ppm is found for (*c,c,c*-CDT) Ni (45, 47) in which the double bonds presumably lie in the trigonal plane. Relatively small coordination shifts appear to be characteristic of complexes formed by cyclic polyenes (bicycloheptadiene is an exception); this phenomenon is also observed for the 1,5-cyclooctadiene complexes discussed later. Coordination chemical shifts for unconstrained polyenes, e.g., $(\text{CH}_2:\text{CHCH}_2)_2\text{NCH}_2\text{CH}:\text{CHCH}_2\text{N}-(\text{CH}_2\text{CH}:\text{CH}_2)_2$, lie in the normal range. A typical example is shown in Fig. 4 (48).

The effect on the coordination chemical shift of varying the phosphine has been studied for two series of trigonal metal-olefin complexes, viz., $(\text{CH}_2:\text{CH}_2)_2\text{PtL}$ (46) and $(\text{CH}_2:\text{C}(\text{CH}_3)\text{CO}_2\text{C}_2\text{H}_5)_2\text{NiL}_2$ (49). In both cases the chemical shift is found to correlate with the basicity of the phosphine [Table IV (41, 45, 46, 49–52)]. The chemical shift of the unsubstituted olefinic carbon atom ($\text{CH}_2:$) of the ethyl methacrylate complexes is more strongly phosphine-dependent than the substituted olefinic carbon atom, and this effect has been attributed to electron withdrawal from this site by the ethoxycarbonyl substituent.

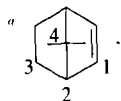
A systematic study of the variation of the olefin on the chemical shift for a series of (olefin) $\text{Ni}[\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-CH}_3)_3]_2$ complexes was mentioned in the introduction to this section (41).

In addition to those complexes listed in Table IV, a number of electron-rich systems involving lithium (53) have been studied, and in these cases unusually large coordination shifts are observed. For example the value

TABLE IV
¹³C-NMR DATA FOR TRIGONAL METAL-OLEFIN COMPLEXES

Complex	Temperature (°C)	Solvent	δC _{olef}	Δδ	¹ J(CH)	Miscellaneous	Reference
(CH ₂ :CH ₂) ₃ Ni	-60	Toluene-d ₈	57.7	-65.5	161(1)		50
(CH ₂ :CH ₂) ₃ Pd	-70	Toluene-d ₈	63.5	-59.7			51
(CH ₂ :CH ₂) ₃ Pt	+20 to -70	C ₆ H ₅ CH ₂ D	48.4	-74.8		J(PtC) 113.0	51
[(CH ₂ :CH ₂) ₂ NiCH ₃] ₂ Li(TMEDA) ₂	-80	Toluene-d ₈	44.2	-79.0	152(1)	-13.5 (δCH ₃)	52
[(CH ₂ :CH ₂) ₂ NiC ₆ H ₅] ₂ Li(TMEDA) ₂	-80	THF-d ₈	45.2	-78.0		21.1, 3.1 (δC ₂ H ₅)	52
			38.4	-84.8			
[(CH ₂ :CH ₂) ₂ NiC ₆ H ₅] ₂ Li(TMEDA) ₂	-77	THF-d ₈	49.3	-73.9		192.2(C _o), 141.8(C _o), 124.0(C _m), 117.5(C _p)	52
			39.3	-83.9			
(CH ₂ :CH ₂) ₂ NiP(C ₆ H ₁₁) ₃	35	THF-d ₈	50.1	-73.1	155(1)		50
(CH ₂ :CH ₂) ₂ PtP(CH ₃) ₃	-80	Toluene-d ₈	37.9	-85.3		J(PtC) 139, J(PC)-7	46
			33.0	-90.2		J(PtC) 158, J(PC) 16	
(CH ₂ :CH ₂) ₂ PtP(CH ₃) ₂ C ₆ H ₅	-80	Toluene-d ₈	39.5	-83.7		J(PtC) 139, J(PC)-6	46
			34.4	-88.8		J(PtC) 159, J(PC) 15	
(CH ₂ :CH ₂) ₂ PtP(C ₆ H ₅) ₂ CH ₃	-80	Toluene-d ₈	42.0	-81.2		J(PtC) 137, J(PC)-6	46
			36.3	-86.9		J(PtC) 156, J(PC) 15	
(CH ₂ :CH ₂) ₂ PtP(C ₆ H ₅) ₃	-80	Toluene-d ₈	45.6	-77.6		J(PtC) 137, J(PC)-5	46
			38.4	-84.8		J(PtC) 154, J(PC) 12	
(CH ₂ :CH ₂) ₂ PtAs(C ₆ H ₅) ₃	-80	Toluene-d ₈	41.6	-81.6		J(PtC) 136	46
			37.1	-86.1		J(PtC) 193	
(CH ₂ :CH ₂)Ni[P(C ₆ H ₁₁) ₃] ₂	R.T.	CD ₂ Cl ₂	37.7	-85.5			41
(CH ₂ :CH ₂)Ni[P(C ₆ H ₅) ₃] ₂	35	Toluene-d ₈	49.7	-73.5			50
(CH ₂ :CH ₂)Ni[P(OC ₆ H ₄ -o-CH ₃) ₃] ₂	R.T.	CD ₂ Cl ₂	47.4	-75.4	160(5)		41
(CH ₂ :CH ₂)Ni[P(C ₆ H ₁₁) ₂ C ₂ H ₄ P(C ₆ H ₁₁) ₂]	R.T.	Toluene-d ₈	32.7	-90.5		J(PC) + J(P'C) 17.1 Hz	50
(Bicycloheptene) ₃ Ni ^a	35	Toluene-d ₈	76.0	-59.4		43.7 (δC ₂), 28.2 (δC ₃), 40.4 (δC ₄)	45
	-60	Toluene-d ₈	76.5	-58.9		43.8, 42.7, 42.6 (δC ₃); 28.2 ₁ , 28.2 ₃ , 28.1 ₈ (δC ₃); 40.3, 40.3 (δC ₄)	
			76.2	-59.3			
			73.1	-62.3			

(Bicycloheptene) ₃ Pt ^a	R.T.	Benzene-d ₆	68.0	-67.4	42.8 (δC ₂), 28.6 (δC ₃), 39.5 (δC ₄)	51
(Bicycloheptene) ₂ NiP(CH ₃) ₃ ^a	35	Toluene-d ₈	69	-67	44.2 (δC ₃), 29.0 (δC ₃), 41.6 (δC ₄)	45
	-60	Toluene-d ₈	64.6	-70.8	44.7, 43.6 (δC ₂), 28.5, 29.4 (δC ₂), 41.6 (δC ₄), J(PC) 6.7, 12.8	
(Bicycloheptene)Ni[PC ₆ H ₅] ₃ ^a	35	Toluene-d ₈	70.7 66.3	-64.7 -69.2	44.6 (δC ₂), 28.8 (δC ₃), 44.1 (δC ₄)	45
(trans-Cyclooctene) ₃ Pt	R.T.	Benzene-d ₆	72.9	-61.1	36.2, 37.1, 29.3 (δ); J(PtC) 154.0	51
(t,t,t-CDT)Ni	35	Toluene-d ₈	106.6	-25.0	146 ± 2 41.2 (δCH ₂)	45
(c,c,c-CDT)Ni	0	Toluene-d ₈	89.0	-41.5	28.8 (δCH ₂)	45
(CH ₂ :CHCN[Ni[P(OC ₆ H ₄ -o-CH ₃) ₃] ₂]	-30	CD ₂ Cl ₂	42.7	-95.1	165(5)	41
			25.9	-82.3	175(5)	
(NCCH:CHCN[Ni[P(OC ₆ H ₄ -o-CH ₃) ₃] ₂]	R.T.	CD ₂ Cl ₂	24.8	-93.0	172(5)	41
(CH ₂ :CHCO ₂ CH ₃)Ni[P(OC ₆ H ₄ -o-CH ₃) ₃] ₂	R.T.	CD ₂ Cl ₂	44.7	-85.2	156(2) 50.2 (δCH ₃), 172.5 (δCO ₂)	41
			52.4	-76.1	160(2)	
(CH ₃ CO ₂ CH:CHCO ₂ CH ₃)Ni[P(OC ₆ H ₄ -o-CH ₃) ₃] ₂	R.T.	CD ₂ Cl ₂	51.1	-78.8	160(2) 49.6 (δCH ₃), 170.7 (δCO ₂)	41
(CH:CHCOOCO)Ni[P(OC ₆ H ₄ -o-CH ₃) ₃] ₂	R.T.	CD ₂ Cl ₂	47.8	-89.3	160(2)	41
(CH ₂ :C(CH ₃)CO ₂ C ₂ H ₅)Ni[P(C ₆ H ₅) ₃] ₂	R.T.	Benzene-d ₆	53.1	-71.5	153.5 19.9 (δCH ₃)	49
			57.6	-79.8		
(CH ₂ :C(CH ₃)CO ₂ C ₂ H ₅)Ni[P(C ₆ H ₅) ₂ C ₂ H ₅] ₂	R.T.	Benzene-d ₆	47.8	-76.8	150.0 20.6 (δCH ₃)	49
			55.1	-82.3		
(CH ₂ :C(CH ₃)CO ₂ C ₂ H ₅)Ni[P(C ₂ H ₅) ₂ C ₆ H ₅] ₂	R.T.	Benzene-d ₆	43.1	-81.5	150.1 20.8 (δCH ₃)	49
			53.4	-84.0		
(CH ₂ :C(CH ₃)CO ₂ C ₂ H ₅)Ni[P(CH ₃) ₂ C ₆ H ₅] ₂	R.T.	Benzene-d ₆	43.0	-81.6	151.5 20.5 (δCH ₃)	49
			54.4	-83.0		
(CH ₂ :C(CH ₃)CO ₂ C ₂ H ₅)Ni[P(C ₂ H ₅) ₃] ₂	R.T.	Benzene-d ₆	40.2	-84.4	152.2 20.6 (δCH ₃)	49
			50.9	-86.5		



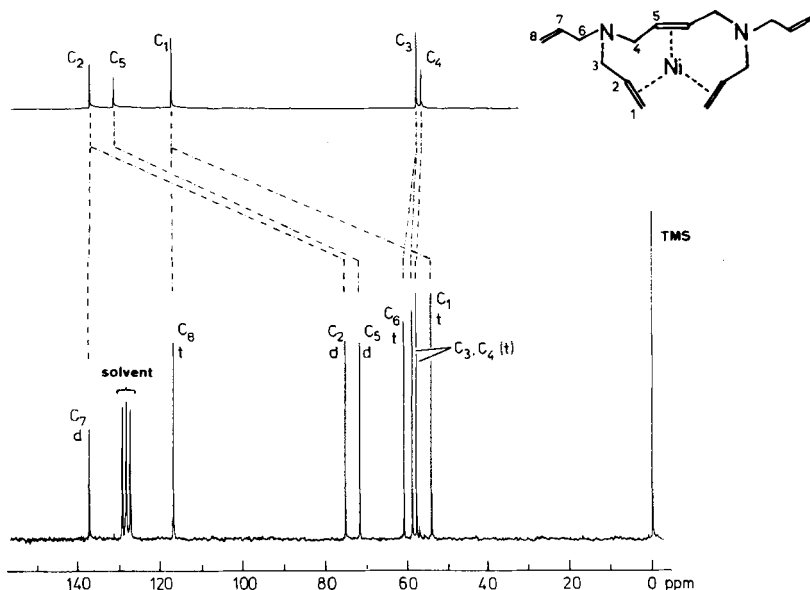


FIG. 4. ^{13}C - $\{^1\text{H}\}$ -NMR spectrum (25.2-MHz) of *trans*- N,N,N',N' -tetrallyl butene-2-diamine-1,4 (insert) and its complex with zerovalent nickel (toluene- d_8 , 30°C). The observation of only eight signals is consistent with C_2 symmetry (48) [δC_1 53.8, δC_2 74.7, δC_3 58.4, δC_4 57.4, δC_5 71.1, δC_6 60.4, δC_7 137.0, δC_8 116.6; $\Delta\delta C_1$ -63.0, $\Delta\delta C_2$ -61.9, $\Delta\delta C_5$ -59.6].

of $\Delta\delta C_{\text{olef}}$ in $(t, t, t\text{-CDT})\text{Ni}[\text{Li}(\text{CH}_3)_2\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$ is -85.1 ppm. This is presumably the result of enhanced back-donation from nickel to the olefin and should be contrasted to the much smaller effects observed for complexes in which back-donation is of minor importance; e.g., $\Delta\delta C_{\text{olef}}$ for $(t, t, t\text{-CDT})\text{Cu}[\text{CF}_3\text{SO}_3]$ is -5.1 ppm (36).

B. Tetrahedral Complexes

$(t, t, t\text{-CDT})\text{Ni}$ is one of the few tris(olefin)nickel complexes which adds a donor ligand. An X-ray structural determination of the trimethylphosphine adduct, $(t, t, t\text{-CDT})\text{NiP}(\text{CH}_3)_3$, has confirmed the pseudo-tetrahedral arrangement of the ligands around the central nickel atom (see 45). The ^{13}C -NMR spectrum of this adduct is shown in Fig. 5, while data for related complexes are collected in Table V. The changes in the chemical shifts of the carbon atoms of the tris-olefin on adduct formation parallel the basicity of the donor ligands. A similar trend is observed for the (1,5-COD) NiL_2 complexes listed in Table VI.

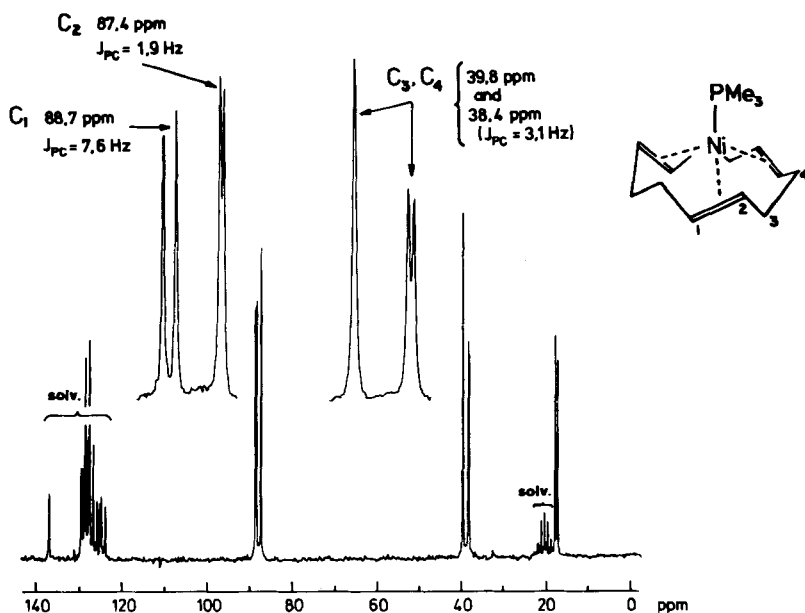


FIG. 5. ^{13}C - $\{^1\text{H}\}$ -NMR spectrum (25.2 MHz) of $(t,t,t\text{-CDT})\text{Ni}(\text{PMe}_3)_3$ (-60°C , toluene- d_8). C_1 and C_2 have been assigned assuming that $|J(\text{PC}_1)| > |J(\text{PC}_2)|$.

C. η^4 -1,3-Diene Complexes

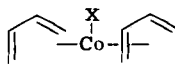
The 1,3-diene-metal complexes show a number of characteristic features and will be treated separately. Data for selected compounds, all containing single-*cis*-butadiene, are collected in Table VII (50, 53–60). Early studies (61) concentrated on differentiating between the two valence bond representations **16** and **17**, while recent interest has centered on intramolecular rearrangements (62).



(16)



(17)



(18)

The $[(\eta^4\text{-butadiene})_2\text{Co}]_n\text{X}$ complexes shown in Table VII have been prepared by reacting $(\text{CH}_2:\text{CH}_2)_4\text{CoK}$ with butadiene and the appropriate metal halide (59). The two butadiene molecules are equivalent and symmetrically bonded to the cobalt atom; one possible structure is **18**. The chemical shift of the central carbon atoms in these complexes falls within a narrow range (77–85 ppm) while that of the terminal carbon atom lies

TABLE V
¹³C-NMR DATA FOR (*t,t,t*-CDT)NiL COMPLEXES^a

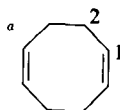
Ligand	Temperature (°C)	Solvent	δC ₁	ΔδC ₁	J(PC ₁)	δC ₂	ΔδC ₂	J(PC ₂)	δC _{3/4}	δC _{4/3}	J(PC _{4/3})
—	35	Toluene- <i>d</i> ₈	106.6	−25.0	—	106.6	−25.0	—	41.2	41.2	—
PF ₃	−20	Toluene- <i>d</i> ₈	97.2	−34.4	9.9	97.1	−34.5	2.4	40.0	36.5	3.9
P(OC ₆ H ₄ - <i>o</i> -C ₆ H ₅) ₃	35	Toluene- <i>d</i> ₈	98.1	−33.5	7.3	94.8	−36.8	—	37.7	36.5	—
P(OC ₆ H ₅) ₃	35	Toluene- <i>d</i> ₈	96.2	−35.4	9.6	93.5	−38.1	3.5	38.2	36.9	3.6
P(C ₆ H ₅) ₃	−50	Toluene- <i>d</i> ₈	94.7	−36.9	4	89.0	−42.6	—	38.7	36.7	—
P(CH ₃) ₃	−60	Toluene- <i>d</i> ₈	88.7	−42.9	7.6	87.4	−44.2	1.9	39.8	38.4	3.1
C ₆ H ₆ ^b	−60	THF- <i>d</i> ₈	86.9	−44.7	—	81.5	−50.1	—	40.4	38.6	—

^a For numbering see Fig. 5; Hoffmann *et al.* (45); C₁/C₂ have been assigned assuming that $|J(PC_1)| > |J(PC_2)|$.

^b Jonas *et al.* (95).

TABLE VI
 ^{13}C -NMR DATA FOR $(1,5\text{-COD})\text{NiL}_2$ COMPLEXES^a

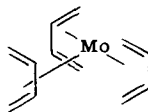
Ligand	Temperature (°C)	Solvent	δC_1	$\Delta\delta\text{C}_1$	δC_2	$\Delta\delta\text{C}_2$
COD	35	Toluene- d_8	89.8	-39.0	30.9	2.4
PF_5	-30	Toluene- d_8	93.8	-35.0	30.0	1.5
$\text{P}(\text{OC}_6\text{H}_4\text{-}o\text{-C}_6\text{H}_5)_3$	35	Toluene- d_8	92.1	-36.6	30.1	1.6
$\text{P}(\text{OC}_6\text{H}_5)_3$	-20	THF- d_8	90.0	-38.7	31.3	2.8
$\text{P}(\text{C}_6\text{H}_{11})_2\text{H}$	35	Toluene- d_8	80.6	-48.2	32.3	3.8
$\text{P}(\text{CH}_3)_3$	35	Toluene- d_8	77.8 ^b	-50.9	31.7	3.2
bipy	35	Toluene- d_8	82.1	-46.6	31.8	3.3
$\text{C}_6\text{H}_5\text{N:NC}_6\text{H}_5$	-20	Toluene- d_8	107.6	-21.1	30.8	2.3
Diethylfumarate	35	THF- d_8	100.6	-28.1	27.5	-1.0
			102.8	-25.9	30.2	1.7
			102.1	-26.6	30.2	1.7



^b $J(\text{PC}_1) \pm 10.0$, ∓ 3.1 ; $J(\text{PP}')$ 4.1.

between 23 and 45 ppm. The observation of the spin-spin coupling between the terminal C atom of the butadiene molecules and the ^{119}Sn nucleus in $(\eta^4\text{-butadiene})_2\text{CoSn}(\text{CH}_3)_3$ ($J = 33$ Hz) establishes the presence of a Co—Sn bond.

An X-ray structural determination of $(\eta^4\text{-butadiene})_3\text{Mo}$ (63) confirms the C_{3h} symmetry (19), and as expected this complex and the tungsten analog give rise to only two absorptions in the ^{13}C -NMR spectrum (60). In the tungsten complex, coupling between ^{183}W and ^{13}C is observed: $J(\text{WC}_1)$ [19.7(5) Hz] is much larger than $J(\text{WC}_2)$ [4.8(5) Hz].

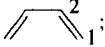


(19)

A comparison of the NMR parameters for $(\eta^4\text{-butadiene})\text{M}(\text{CO})_3$ (where M is Fe or Ru), carried out by von Philipsborn and co-workers (54, 55), provides an excellent example of the potential of a complete spectral analysis (Fig. 6). Values for the vicinal C—H and H—H couplings have been extracted and used to deduce the conformation of the complexed ligand. The authors conclude that the carbon skeleton is coplanar, that the

TABLE VII
¹³C-NMR DATA FOR (η⁴-BUTADIENE)M COMPLEXES^a

Complex	Temperature (°C)	Solvent	δC ₁	ΔδC ₁	δC ₂	ΔδC ₂	¹ J(C ₁ H)	¹ J(C ₂ H)	Reference
(η ⁴ -Butadiene)Fe(CO) ₃	—	Benzene- <i>d</i> ₆	40.5	-77.2	85.5	-52.6	161.5, 156.2	169.1	54
(η ⁴ -Butadiene)Ru(CO) ₃	—	Benzene- <i>d</i> ₆	32.7	-85.0	86.3	-51.8	156.2 159.6	168.2	55
(η ⁴ -Butadiene)Cr(CO) ₄	-20	Toluene- <i>d</i> ₈	56.5	-61.2	86.5	-51.6			55a
(η ⁴ -Butadiene)Ti(COT)	35	Toluene- <i>d</i> ₈	69.7	-48.1	111.4	-26.7	155(2)	161(3)	50, 56
(η ⁴ -Butadiene)Zr(COT)	35	Toluene- <i>d</i> ₈	54.6	-63.2	115.8	-22.3			50, 56
(η ⁴ -Butadiene)Hf(COT)	35	Toluene- <i>d</i> ₈	50.5	-67.3	116.3	-21.9	146(2)	156(4)	50, 56
[(η ⁴ -Butadiene)Cr] ₃ COT	0	Toluene- <i>d</i> ₈	55.5	-62.3	103.0	-35.1			57
(η ⁴ -Butadiene)Zr (CH ₃) ₂ PCH ₂ CH ₂ P(CH ₃) ₂	—	—	39.1	-78.6	105.6	-32.5	146	156	58
(η ⁴ -Butadiene) ₂ Mo(CO) ₂	-85	Toluene- <i>d</i> ₈ /CS ₂	{ 43.4 45.0	{ -74.3 -72.7	{ 69.4 92.9	{ -68.7 -45.2			55a
(η ⁴ -Butadiene) ₂ CoSn(CH ₃) ₃ ^b	-60	Toluene- <i>d</i> ₈	41.7	-76.0	79.4	-58.7			59
[(η ⁴ -Butadiene) ₂ Co] ₂ Zn	35	Toluene- <i>d</i> ₈	25.0	-92.7	82.5	-55.6	154	166	59
(η ⁴ -Butadiene) ₂ CoLi(CH ₃) ₂ NC ₂ H ₄ N(CH ₃) ₂	35	Toluene- <i>d</i> ₈	23.1	-94.6	79.8	-58.3	146	162(1)	50, 53
	-80	Toluene- <i>d</i> ₈	{ 18.2 28.2	{ -99.5 -89.5	{ 80.8 79.1	{ -57.3 -59.0	140(2) 152(2)	162(2) 161(2)	50, 53
(η ⁴ -Butadiene) ₃ Mo	35	Benzene- <i>d</i> ₆	41.4	-76.3	102.2	-35.9	155(2)	164(3)	60
(η ⁴ -Butadiene) ₃ W	35	Benzene- <i>d</i> ₆	33.7	-84.0	103.4	-34.7	152(2)	164(3)	60

^a ; δC₁ 117.7, δC₂ 138.1 (30°C, CDCl₃).

^b *J*(¹¹⁹SnC) 33 Hz.

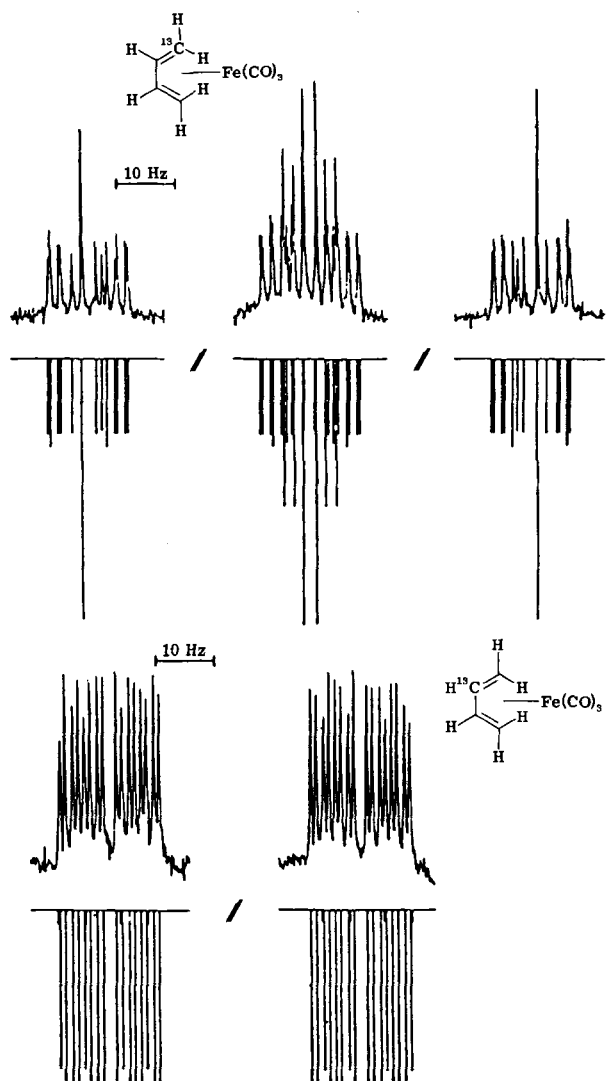


FIG. 6. Experimental and calculated proton coupled ^{13}C -NMR spectra (25.2 MHz) of $(\eta^4\text{-butadiene})\text{Fe}(\text{CO})_3$ (54).

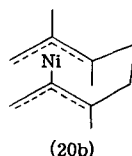
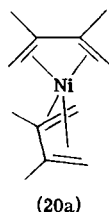
C—C bond lengths are practically identical, and that the carbon atoms are essentially sp^2 -hybridized. A small rehybridization toward sp^3 of the terminal C atoms introduces the slight torsion necessary to optimize overlap of the ligand π -orbitals with the metal d-orbitals.

Examination of the data shown in Table VII allows the following generalizations: (1) the coordination chemical shift of the terminal carbon atoms (C_1) is always greater (and can be 2–3 times larger) than that of the central carbon atoms (C_2); and (2) the coupling constant $^1J(\text{CH})$ for the terminal carbon atom lies typically in the range 150–160 Hz, and that for the central carbon atom is somewhat larger (160–170 Hz). If the ratio of the coordination chemical shifts $\Delta\delta C_1/\Delta\delta C_2$ is defined as ρ , then for a series of complexes ρ increases on descending a period, e.g.,

$(\eta^4\text{-butadiene})\text{M}(\text{CO})_3$	M	Fe	Ru	Os
	ρ	1.47	1.65	1.68
$(\eta^4\text{-butadiene})_3\text{M}$	M	Mo	W	
	ρ	2.14	2.44	
$(\eta^4\text{-butadiene})\text{M}(\text{COT})$	M	Ti	Zr	Hf
	ρ	1.8	2.9	3.1

Even in $(\eta^4\text{-butadiene})\text{Hf}(\text{COT})$ —the complex having the largest ρ -value and smallest $\Delta\delta C_2$ value—the -21.6 ppm coordination shift for C_2 clearly indicates that the butadiene is still acting as an η^4 -ligand. The abnormally low value of 146(2) Hz for $^1J(\text{C}_1\text{H})$ [$^1J(\text{C}_2\text{H})$ is 156(4) Hz] suggests, however, that the metal is interacting more strongly with the terminal carbon atoms than with the central atoms and that resonance form **17** has greater weight in this compound. This is also reflected in the fluxionality observed in the PMR spectrum (64). The ^{13}C -NMR data for $(\eta^4\text{-C}_4\text{H}_6)_2\text{Zr}(\text{CH}_3)_2\text{-PC}_2\text{H}_4\text{P}(\text{CH}_3)_2$ have been similarly interpreted (58).

In addition to the complexes listed in Table VII, we have used ^{13}C NMR to determine the structure of the product of the reaction of $(\text{CDT})\text{Ni}$ with 2,3-dimethylbutadiene (65). The spectrum (-40°C) consists of six signals—two unprotonated carbon atoms at 102.3 and 101.7 ppm, two methylene carbon atoms at 61.1 and 48.4 ppm, and two methyl carbon atoms at 21.8 and 19.4 ppm. A determination of $^1J(\text{CH})$ for the methylene C atoms gave values of 156 and 157 Hz (both ± 3 Hz), clearly indicating that they are both sp^2 -hybridized and thereby eliminating structures such as **20b**. The spectrum is consistent with a pseudotetrahedral arrangement of the two diene molecules about the nickel atom (**20a**).



IV

 η^3 -ALLYL METAL COMPLEXES

In view of the important role played by PMR spectroscopy in determining the structure and the mode of rearrangement of the η^3 -allyl metal complexes, it is surprising that the ^{13}C -NMR spectra of relatively few examples have been reported. Complexes of this type are of considerable interest as intermediates in the metal-catalyzed transformations of 1,3-dienes, and we have recently systematically investigated a number of systems. Selected examples will be discussed.

The bis(η^3 -allyl)metal complexes can exist in at least two forms which differ in the mutual orientation (cis or trans) of the two allyl groups. Although no direct evidence for the cis arrangement has been obtained, the trans arrangement has been shown crystallographically to be present in $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$ and $(\eta^3\text{-pinenyl})_2\text{Ni}$ (66, 67). The presence of two isomers for the simple $(\eta^3\text{-C}_3\text{H}_5)_2\text{M}$ complexes of nickel, palladium, and platinum has been confirmed by ^{13}C -NMR spectroscopy (Fig. 7; 47, 68). Additional isomers are possible for complexes having substituents on the terminal carbon atoms; this is illustrated in Fig. 8 for $(\eta^3\text{-1,1-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$, while data for selected complexes are collected in Table VIII.

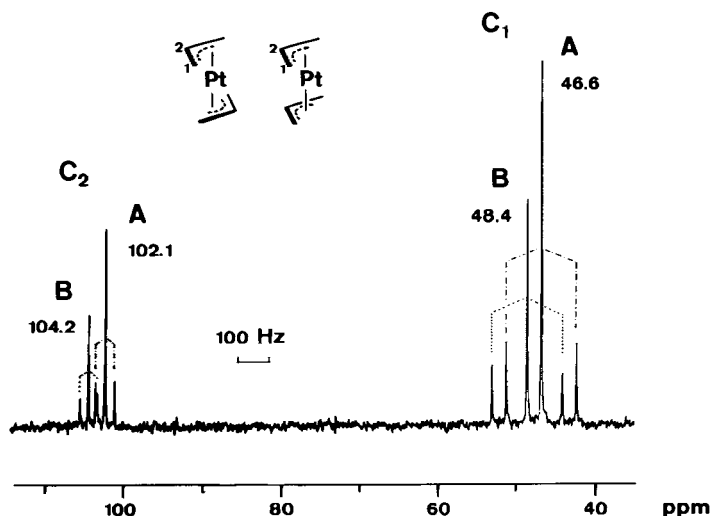


FIG. 7. ^{13}C - $\{^1\text{H}\}$ -NMR spectrum (25.2 MHz) of $(\eta^3\text{-C}_3\text{H}_5)_2\text{Pt}$ (9°C , $\text{toluene-}d_8$). The satellites are due to coupling with ^{195}Pt (33.7% natural abundance): A (trans) $J(\text{PtC}_1) = 225.2$, $J(\text{PtC}_2) = 61.1$ Hz; B (cis) $J(\text{PtC}_1) = 226.0$, $J(\text{PtC}_2) = 54.5$ Hz.

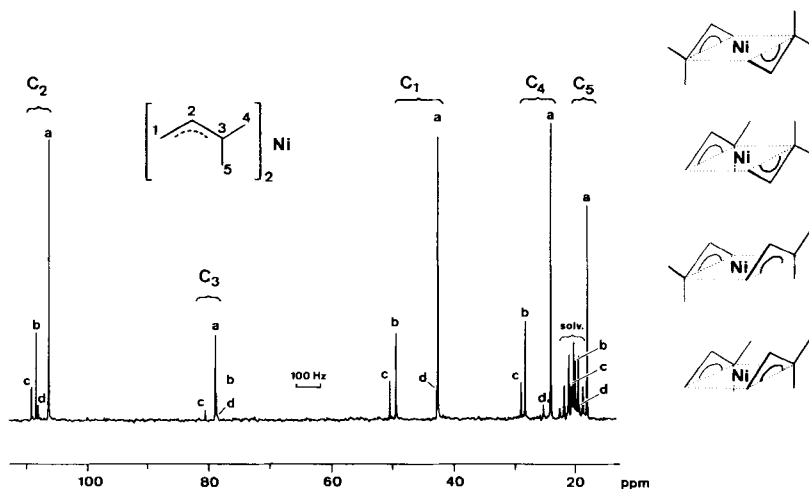


FIG. 8. $^{13}\text{C}\{-^1\text{H}\}$ -NMR spectrum (25.2 MHz) of $(\eta^3\text{-}1,1\text{-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$ (-20°C , toluene- d_8). The sample is a mixture of the four possible isomers a-d (67, 21, 9, and 4%, respectively).

The position of the resonances for the meso carbon atom generally falls in the range 128–102 ppm, while those for the terminal carbon atoms are found at 86–42 ppm. This is in qualitative agreement with the molecular orbital view of the bonding in these systems in which the strongest interaction is between the metal and the ψ_2 orbital of the η^3 -allyl group. Inspection of the data in Table VIII indicates that for a given allyl group the chemical shifts of both the meso and terminal carbon atoms decrease in the order $\text{Pd} > \text{Ni} > \text{Pt}$. An adequate explanation for this phenomenon has yet to be offered.

A second group of complexes that have received detailed attention are the $(\eta^3\text{-allyl})\text{nickel}(\eta^5\text{-cyclopentadienyl})$ complexes, which may be prepared by reacting nickelocene with an allyl-Grignard reagent (69). Data for typical examples are shown in Table IX. In this particular case, a sufficiently large number of complexes have been studied that a series of chemical shift increments can be extracted from the data (shown in Table X) and have been used with considerable success in assigning structures to η^3 -allyl nickel complexes of unknown structure.

In addition to the η^3 -allyl complexes of nickel, palladium, and platinum, we have also examined $(\eta^3\text{-allyl})_3\text{Rh}$ and the $(\eta^3\text{-allyl})_4\text{M}$ complexes of Zr, Mo, and W (70). The data for these complexes are collected in Table XI.

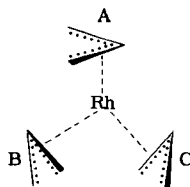
The spectrum of $(\eta^3\text{-C}_3\text{H}_5)_3\text{Rh}$ at -75°C (25 MHz) consists of six signals: three for the terminal carbon atoms and three for the meso carbon

TABLE VIII
 ^{13}C -NMR DATA FOR TYPICAL $(\eta^3\text{-ALLYL})_2\text{M}$ COMPLEXES
 OF NICKEL, PALLADIUM, AND PLATINUM (68)^a

Complex	Temperature (°C)	%	δC_1	δC_2	δC_3	δCH_3
$(\eta^3\text{-C}_3\text{H}_5)_2\text{Ni}$	-24	A 70	52.6	112.1	52.6	
		B 30	53.0	112.2	53.0	
Pd	0	A 73	54.6	115.1	54.6	
		B 27	53.8	115.5	53.8	
Pt ^b	9	A 63	46.6	102.1	46.6	
		B 37	48.4	104.2	48.4	
$(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	0	A 70	51.1	122.8	51.1	24.4
		B 30	51.8	123.9	51.8	24.4
Pd	10	A 67	53.6	128.1	53.6	24.7
		B 33	53.0	127.9	53.0	24.9
Pt	32	A ^c 60	45.9	115.5	45.8	24.7
		B ^d 40	47.5	117.2	47.5	24.7
$(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	-60	A 55	71.1	112.5	46.0	17.2
		B 25	68.7	113.7	50.2	19.7
		C 15	69.4	112.1	— ^e	17.1
		D 5	68.0	112.9	49.9	— ^e
Pd	-20	A 55	75.6	115.4	47.0	17.6
		B 25	72.1	116.0	46.7	17.3
		C 20	72.2	116.6	52.2	20.2

^a Toluene-*d*₈. ^b See Fig. 7. ^c $J(\text{PtC}_1) = 220.3$; $J(\text{PtC}_2) = 71.2$; $J(\text{PtCH}_3) = 34.8$ Hz.
^d $J(\text{PtC}_1) = 223.3$; $J(\text{PtC}_2)$ nd; $J(\text{PtCH}_3) = 34.8$ Hz. ^e Obscured by other resonances.

atoms. On raising the temperature, two signals remain sharp (those at 48.2 and 100.2 ppm) while the others initially broaden and then coalesce at room temperature to give two additional sharp absorptions. These results are fully consistent with the interpretation of the PMR spectrum given by Becconsall and O'Brien (71): the complex is suggested to have structure **21** and the observed exchange to be the result of rotation of either group A or B about the allyl-metal axis.



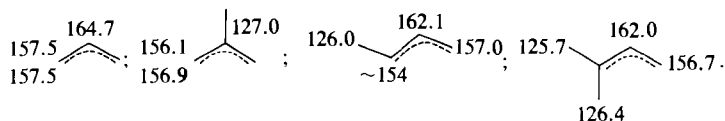
(21)

TABLE IX
 ^{13}C -NMR DATA FOR TYPICAL $(\eta^3\text{-ALLYL})\text{Ni}(\eta^5\text{-C}_5\text{H}_5)$ COMPLEXES (50,69)^{a,b}

Allyl group	δC_1	δC_2	δC_3	δCH_3	$\delta\text{C}_5\text{H}_5$
	39.8	90.9	39.9	—	88.6
	42.1	106.8	42.1	23.7	88.8
	58.1	92.0	35.9	20.8	89.1
	56.2	90.9	38.2	16.3	89.1
	71.9	91.4	35.4	30.3 (syn) 22.6 (anti)	89.3
	54.0	94.2	54.0	20.4	89.2
	55.8	92.9	51.8	21.0 (syn) 17.2 (anti)	89.1

^a 35°C, toluene-*d*₈.

^b $^1J(\text{CH})$ (± 0.2 Hz):



The spectra of the tetra- η^3 -allyl complexes of Mo, W, and Zr (Table XI) show significant differences. Whereas that of the zirconium complex has only two signals (one for the meso and one for the terminal carbon atoms), the spectra of the molybdenum and tungsten complexes consist of three

TABLE X
 ^{13}C -CHEMICAL SHIFT INCREMENTS FOR METHYL SUBSTITUTION
 IN $(\eta^3\text{-ALLYL})\text{Ni}(\eta^5\text{-C}_5\text{H}_5)$ COMPLEXES (50)^{a,b}

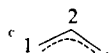
CH_3 substituent	$\Delta\delta\text{C}_1$	$\Delta\delta\text{C}_2$	$\Delta\delta\text{C}_3$
syn at C_1	17.9	2.1	-4.3
syn at C_1 (<i>anti</i> -methyl present)	14.6	0.4	-1.6
anti at C_1	15.9	-0.5	-1.5
anti at C_1 (<i>syn</i> -methyl present)	13.6	-0.7	0.0
anti at C_2 (syn = H,H)	1.9	14.1	1.9
anti at C_2 (syn = H,R)	0.0	13.8	3.8

^a $\Delta\delta\text{C}_n = \delta\text{C}_n$ (substituted allyl) - δC_n (unsubstituted allyl).



TABLE XI
 ^{13}C -NMR DATA FOR THE η^3 -ALLYL COMPLEXES OF Rh, Mo, W, AND Zr^a

Complex	Temperature (°C)	Solvent	δC_1	$J(\text{MC})$	$^1J(\text{CH})$	δC_2	$J(\text{MC})$	$^1J(\text{CH})$
$(\eta^3\text{-C}_3\text{H}_5)_3\text{Rh}$	30	Toluene- d_8	48.3	8.8		100.3	4.3	
			41.3 ^b	9.0		95.2 ^b	4.5	
	-75	Toluene- d_8	48.2	8.8		100.2	4.5	
			41.6	~8		94.9	4.5	
			40.3	8.7		94.2	4.1	
$(\eta^3\text{-C}_3\text{H}_5)_3\text{Mo}$	30	Benzene- d_6	48.8		159(1)	102.9		154(1)
			66.4		153(1)			
$(\eta^3\text{-C}_3\text{H}_5)_3\text{W}$	30	Toluene- d_8	43.3	7.4	160(1)	99.4	nd	156(1)
			61.5	13.8	152(1)			
$(\eta^3\text{-C}_3\text{H}_5)_3\text{Zr}$	-60	Toluene- d_8	65.0 ^c		153(1)	138.9		148(1)

^a From Biermann *et al.* (70).^b Intensity = 2.

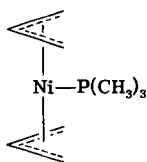
signals in the ratio 1 : 1 : 1, suggesting that here the allyl groups are equivalent but not symmetrical. These results are consistent with a tetrahedral arrangement of the allyl groups about the central metal atom which, in the case of the molybdenum and tungsten complexes, is distorted as a result of twist about the metal-allyl axis.

The bis(η^3 -allyl)nickel complexes form adducts with tertiary phosphines in which the allyl groups are mutually cis (30). This arrangement has been confirmed by crystal structure analysis for $(\eta^3\text{-C}_3\text{H}_5)_2\text{NiP}(\text{CH}_3)_3$ (22) and by comparing the ^{13}C -NMR spectral data with those of the related complex $(\eta^3, \eta^3\text{-C}_9\text{H}_{12})\text{NiP}(\text{CH}_3)_3$ (23) formed by reacting allene with bis(1,5-cyclooctadiene)nickel in the presence of the phosphine. The data for this complex are shown in Table XII and those for representative $(\eta^3\text{-allyl})_2\text{NiPR}_3$ complexes in Table XIII.

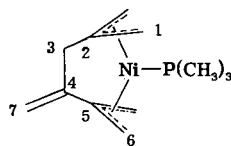
 TABLE XII
 ^{13}C -NMR DATA FOR $(\eta^3, \eta^3\text{-C}_9\text{H}_{12})\text{NiP}(\text{CH}_3)_3$ (23)

C_n	C_1	C_2	C_3	C_4	C_5	C_6	C_7	CH_3
δC_n	47.5	106.3	43.6	152.6	113.1	46.2	109.3	18.5
$J(\text{PC})$	nd	6.1	1.3	0.6	6.4	—	5.8	19.4
Multiplet	t	s	t	s	s	t	t	q
$^1J(\text{CH})$	156	—	—	—	—	157	156	128

^a Mynott (50).^b Toluene- d_6 at 35°C.



(22)



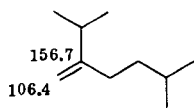
(23)

In the spectrum of complex **23** it is remarkable that the unsymmetrical bonding of the η^3 -allyl groups, which has been observed crystallographically in the corresponding tricyclohexylphosphine complex (**72**), is not maintained in solution. Particularly significant is the lack of coupling between the phosphorus atom and the terminal carbon atoms (C_1 , C_8) and the unusually large coupling to the meso carbon atoms (C_2 , C_5). This is in contrast to the situation found for the square planar η^3 -allyl-Ni(X)L complexes (see p. 290) but is also observed in the $(\eta^3\text{-allyl})_2\text{NiPR}_3$ complexes. The chemical shifts for the olefinic carbon atoms (C_4 , C_7) are similar to those observed for the related olefin **24** and estimated for **25**, suggesting that there is no significant interaction between the *exo*-methylene group and the allyl group.

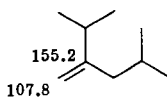
TABLE XIII
 ^{13}C -NMR DATA FOR $(\eta^3\text{-ALLYL})_2\text{NiPR}_3$ COMPLEXES^{a,b}

Allyl group	Phosphine	Temperature (°C)	δC_1	δC_2	$J(\text{PC}_2)$	δC_3	δCH_3
	$\text{P}(\text{CH}_3)_3$	-60	41.7	91.5	6.7	41.7	—
	$\text{P}(\text{C}_6\text{H}_{11})_3$	-30	42.5 ^c	95.8 ^d	nd ^e	42.5	—
	$\text{P}(\text{C}_6\text{H}_5)_3$	-60	45.8	96.3	4.3	45.8	—
	$\text{P}(\text{CH}_3)_3$	-80	42.9 ^f	105.3	7.8	42.9	24.3 ^g
	$\text{P}(\text{CH}_3)_3$	-80	51.8	94.1	5.9	51.8	18.6
	$\text{P}(\text{CH}_3)_3$	-40	57.7	93.5	6.4	41.7 ^h	19.7

^a From Henc *et al.* (30). ^b Toluene- d_8 . ^c $^1J(\text{CH})$ 155(2) Hz. ^d $^1J(\text{CH})$ = 156.9(0.5) Hz. ^e Not observed (phosphine exchange). ^f $^1J(\text{CH})$ = 153(2) Hz. ^g $J(\text{PC}_4)$ 3.7 Hz. ^h $J(\text{PC})$ 2.4 Hz.



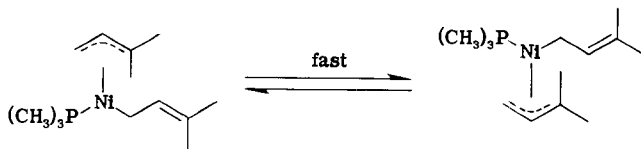
(24)



(25)

The data for the $(\eta^3\text{-allyl})_2\text{NiPR}_3$ complexes shown in Table XIII have been obtained at low temperature: at higher temperatures partial dissociation with rapid exchange of the phosphine takes place. This is illustrated for $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{NiP}(\text{C}_6\text{H}_5)_3$ in Table XIV; at room temperature dissociation is practically complete. Comparison of the chemical shifts of the corresponding bis($\eta^3\text{-allyl}$)nickel complexes with those of the trialkylphosphine adducts shows that adduct formation is accompanied by high field shifts of the meso carbon atoms of 18–20 ppm and of the terminal carbon atoms of 8–11 ppm. In the case of the $\text{P}(\text{C}_6\text{H}_5)_3$ adducts these values are approximately 13 and 5 ppm, respectively.

In contrast to the other nickel complexes discussed here, that formed by $(\eta^3\text{-1,1-(CH}_3)_2\text{C}_3\text{H}_3)_2\text{Ni}$ with $\text{P}(\text{CH}_3)_3$ has the 16-electron structure **26** in which fast $\eta^1 \leftrightarrow \eta^3\text{-allyl}$ exchange occurs even at -95°C . As a result of



(26)

TABLE XIV
VARIATION OF THE ^{13}C -NMR PARAMETERS OF
 $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{NiP}(\text{C}_6\text{H}_5)_3$ WITH TEMPERATURE^{a,b}

Temperature ($^\circ\text{C}$)	δC_1	δC_2	δCH_3	δC_4	$ ^1J(\text{PC}) $
-75	46.5	109.9	24.8	134.9	21.2
-50	46.8	111.4	24.6	135.4	18.1
-10	48.8	116.7	24.5	136.6	4.6
34	50.8	122.2	24.3	137.7	12.9
Uncomplexed $(\eta^3\text{-2-CH}_3\text{C}_3\text{H}_4)_2\text{Ni}$	{ 51.1 ^c 51.8	{ 122.8 123.9	{ 24.4 24.4	{ 137.2	{ 12.5

^a From Henc *et al.* (30).

^b ; 25.2 MHz in toluene- d_8 .

^c Cis and trans isomers.

this exchange, only five absorptions are observed for the carbon atoms of the organic ligands. However, the value for $^1J(C_1H)$ of 141 Hz (intermediate between those expected for η^1 - and η^3 -allyl carbon atoms) and changes in the chemical shift upon adduct formation (in contrast to the 18-electron adducts discussed earlier, formation of **26** results in a shift of the absorption for the meso carbon atoms of 7 ppm to lower field, for the unsubstituted terminal carbon atoms of 11 ppm to higher field, and for the disubstituted terminal carbon atoms of 15 ppm to lower field) clearly indicate that isomerization of one η^3 -allyl group has occurred. Related platinum and palladium complexes were mentioned in Section II.

It is appropriate to include here two bis(η^3 -allyl)nickel complexes that are formed by reacting zerovalent nickel species with 1,3-dienes and that have been shown to be involved as intermediates in the nickel-catalyzed cyclooligomerization of butadiene, viz., $(\eta^3, \eta^3-C_{12}H_{18})Ni$ and $(\eta^3-C_8H_{12})NiPR_3$.

It has been known for many years that the key intermediate in the cyclotrimerization of butadiene to 1,5,9-cyclododecatriene is an η^3, η^3 -dodecatrienediyl nickel species (**73**). We have recently reinvestigated this complex in the hope of obtaining further structural information, and the ^{13}C -NMR spectrum is shown in Fig. 9. The spectra in THF- d_8 and toluene- d_8 are practically identical, indicating that THF is not here functioning as a ligand. The spectrum shown in Fig. 9 was run in THF- d_8 and

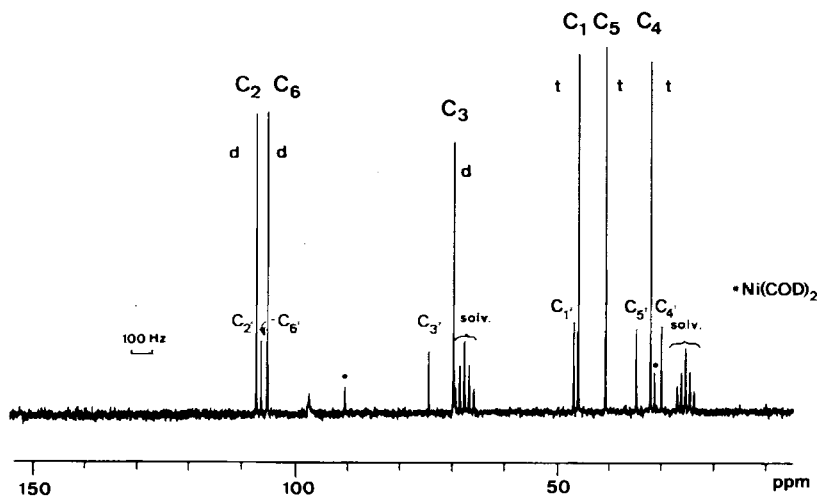


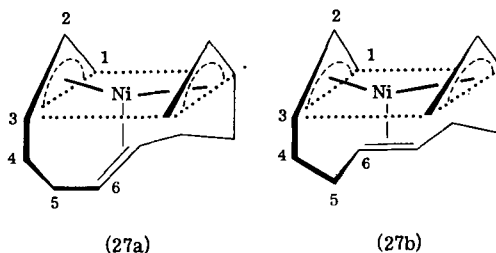
FIG. 9. ^{13}C - $\{^1H\}$ -NMR spectrum (25.2 MHz) of η^3, η^3 -dodecatrienediylnickel (**68**) ($0^\circ C$, THF- d_8). [Toluene- d_8 , $-60^\circ C$: δC_1 45.0, δC_2 106.2, δC_3 69.1, δC_4 31.7, δC_5 40.5, δC_6 105.1; δC_1 , 46.5, δC_2 , 105.3, δC_3 , 73.7, δC_4 , 29.0, δC_5 , 33.9, δC_6 , 103.3.]

demonstrates the absence of signals around 130 ppm. Assignment of the resonances is unambiguous and is supported by selective proton-decoupling experiments. The following conclusions can be drawn from the spectra.

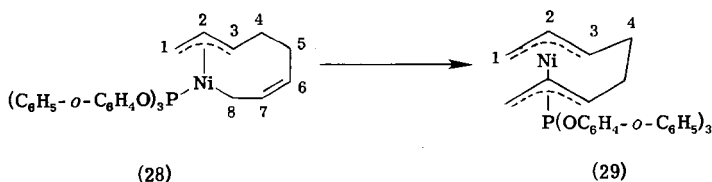
1. The C_{12} chain of the major component is bonded symmetrically to the metal atom since only six absorptions for the 12 carbon atoms are observed.
2. A second isomer ($\sim 20\%$) is present which also has a symmetrical structure.
3. The double bond is complexed to the nickel atom. The estimated up-field shift of approximately 25 ppm is, however, relatively small for zero-valent nickel olefin complexes.
4. The complexed double bond has a trans configuration. The chemical shift of C_5 (major component) is 40.5 ppm: in a cis configuration it would be expected that the γ -interaction between the *cis*-methylene groups at C_5 would cause a shift of this signal to approximately 30 ppm.

The PMR spectrum indicates that the η^3 -allyl groups in both components are anti-substituted and provides further evidence for the trans configuration of the complexed double bond.

The structures most consistent with the spectroscopic data are **27a** and **27b**. These can be formally interconverted by rotation of the complexed double bond. Although two other arrangements are possible, models indicate that they are strained and hence less probable.



The key intermediate in the cyclodimerization of butadiene using a ligand-modified zerovalent nickel catalyst is an $(\eta^3\text{-C}_8\text{H}_{12})\text{NiL}$ system whose configuration depends upon the nature of the ligand attached to nickel (74). A ^{13}C -NMR investigation has shown that the initial complex that forms is an $\eta^1, \eta^3\text{-C}_8\text{H}_{12}\text{NiL}$ complex (e.g., **28**) which, where L is a triarylphosphite or -phosphine, rearranges irreversibly to a symmetrical $\eta^3, \eta^3\text{-C}_8\text{H}_{12}\text{NiL}$ system (e.g., **29**). Complex **29** reacts further by ring closure to give (1,5-cyclooctadiene)nickel species.



The ^{13}C -NMR spectra illustrating this sequence are shown in Fig. 10. Typical for **28** is the low-field absorption of the nickel-bonded methylene group (C_8) and the coupling to phosphorus [$J(\text{PC}_8) = 18.4 \text{ Hz}$] as well as the large P—C coupling [$J(\text{PC}_3) = 30.9 \text{ Hz}$] between the carbon atom (C_3) of the η^3 -allyl group trans to phosphorus. The formulation of **29** as having a structure in which the η^3 -allyl groups are syn-substituted and in which the phosphite is "trans" to the meso carbon atoms should be regarded as provisional but is supported by chemical shift increment data and by the observation of values for $J(\text{PC}_1)$, $J(\text{PC}_2)$, and $J(\text{PC}_3)$ almost

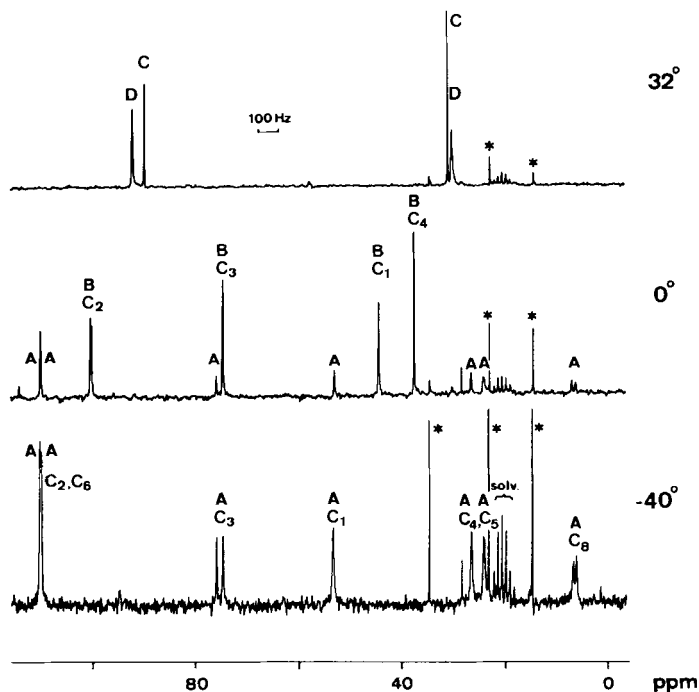


FIG 10. The rearrangement of $\eta^3\text{-C}_8\text{H}_{12}\text{NiP(OC}_6\text{H}_4\text{-}o\text{-}\text{C}_6\text{H}_5)_3$ (25.2 MHz, toluene- d_8). The absorptions labeled A, B, C, and D are due to **28**, **29**, $(\text{COD})_2\text{Ni}$, and $(\text{COD})\text{NiL}_2$, respectively (* = pentane).

TABLE XV
¹³C-NMR DATA FOR (η³-cyclo-C₈H₁₃)Ni(Br)L COMPLEXES^{a,b}

Complex	Temperature (°C)	δC ₁	J(PC ₁)	δC ₂	J(PC ₂)	δC ₃	J(PC ₃)
(η ³ -C ₈ H ₁₃ NiBr) ₂	35	70.7	—	103.3	—	70.7	—
η ³ -C ₈ H ₁₃ Ni(Br)P(CH ₃) ₃	−30	62.5	5.0	106.9	1.1	85.6	23.6
η ³ -C ₈ H ₁₃ Ni(Br)P(C ₆ H ₁₁) ₃	35	61.9	4.9	106.9	0.9	86.2	20.9
η ³ -C ₈ H ₁₃ Ni(Br)P(C ₆ H ₅) ₃	−30	70.1	nd	107.8	0.9	86.6	21.6
η ³ -C ₈ H ₁₃ Ni(Br)P(OCH ₃) ₃	−30	67.1	4.3	108.7	4.2	90.5	33.6
η ³ -C ₈ H ₁₃ Ni(Br)P(O- <i>i</i> -C ₃ H ₇) ₃	−40	67.1	4.8	108.4	3.7	89.5	32.8
η ³ -C ₈ H ₁₃ Ni(Br)P(OC ₆ H ₅) ₃	−30	69.2	2.8	109.6	4.9	92.1	35.9
η ³ -C ₈ H ₁₃ Ni(Br)P(OC ₆ H ₄ - <i>o</i> -C ₆ H ₅) ₃	35	69.4	3.2	108.8	5.2	92.5	36.9

^a From Mynott (50) and Berger (75).

^b 25.2 MHz, toluene-*d*₆; geometry of C₈ ring, see Fig. 1; PR₃ trans to C₃.

identical with those observed for $(\eta^3\text{-1-CH}_3\text{C}_3\text{H}_4)_2\text{NiP(CH}_3)_3$, i.e., ≈ 0 , 6.4, and 2.4 Hz, respectively.

In addition to the complexes already discussed in this section, we have investigated a series of $(\eta^3\text{-cyclooctenyl})\text{Ni(Br)L}$ complexes in order to study the effect of the nature of the ligand upon the NMR parameters (75). Typical results are shown in Table XV. Complexation of a tertiary phosphite or phosphine to $(\eta^3\text{-cyclooctenyl})\text{NiBr}_2$ is accompanied by a high field shift of the meso carbon atom (C_2) and the terminal carbon atom trans to the ligand (C_3) and by a low field shift of C_1 (cis to L). The values for the chemical shifts of C_2 and C_3 follow the order

$$\text{P(Oaryl)}_3 > \text{P(Oalkyl)}_3 > \text{P(C}_6\text{H}_5)_3 > \text{P(alkyl)}_3$$

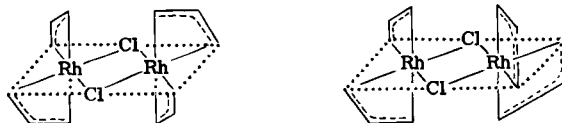
and reflect the trans influence of the ligand. Characteristic is the difference between $J(\text{PC}_3)$ (trans) and $J(\text{PC}_1)$ (cis): the trans coupling lies in the range 32–37 Hz for phosphite complexes and 21–24 Hz for phosphine complexes while the cis coupling has a value of 3–5 Hz. The meso coupling constants have values of approximately 1 Hz for the phosphine complexes and 4–5 Hz for the phosphites.

V

CHIRAL COMPLEXES

Chiral complexes are a rewarding field of study for ^{13}C -NMR investigations. The sensitivity of the ^{13}C atoms to the local environment is usually sufficient to allow the resolution and identification of the individual diastereomers, and although the magnitude of the splitting may appear to provide no direct chemical information, their very observation does.

Diastereomeric complexes are not uncommon in organometallic chemistry. For example, $[(\eta^3\text{-allyl})_2\text{RhCl}]_2$ occurs as diastereomers (30) which give rise to two sets of signals in the ^{13}C -NMR spectrum. Interestingly,

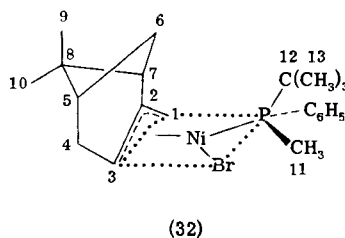
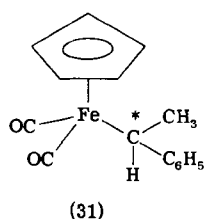


(30)

the compound of this type involving $\eta^3\text{-(+)-(1R,5R)}$ -pinenyl gives rise to only one set of signals, indicating that in this case only one of the possible enantiomers is formed.

The nonequivalence of diastereotopic carbon atoms is frequently observed. For example, the carbonyl ligands in **31** give rise to two signals at 217.1 and 217.5 ppm in the NMR spectrum (76)¹ Similar nonequivalence of the cyclohexyl carbon atoms is also frequently observed in the spectra of complexes involving cyclohexylphosphine ligands (see Table XVII and Fig. 14).

Behrens and Wilke (77) have described a method for resolving enantiomeric Horner phosphines ($\text{PR}_1\text{R}_2\text{R}_3$) by complexation with η^3 -(+)-(1*R*,5*R*)-pinenyl nickel bromide dimer: a 1:1 adduct is formed, purified by recrystallization, and the optically pure phosphine released by reaction with excess trimethylphosphine. The geometry of the adduct **32** formed by methyl-*tert*-butylphenyl phosphine is shown here. The ^{13}C -NMR spectrum



of a mixture of both diastereomeric adducts [(*R*)- and (*S*)-phosphine] has been examined. Each component gives rise to 17 signals, all of which have been resolved and assigned (Table XVI). One component is identical to that whose absolute configuration has been determined by X-ray crystallography (78).

The assignment itself is relatively straightforward. Perhaps the most remarkable feature of these spectra is that *all* signals give an observable diastereomeric splitting. Measurement of the relative intensities of the phosphorus-methyl signals (C_{11}) provides a good, relatively quick, and reliable method for determining the optical purity of the phosphine. (The ^{31}P -NMR spectra of this and similar complexes proved less satisfactory since all the signals were relatively broad and the splittings small.) The fact that virtually all the carbon signals are split and have the same relative intensities confirms that the signals do indeed come from two diastereomers and not, for example, from an impurity.

An even more complicated example is to be found in complexes of the type $(\eta^3\text{-allyl})\text{Ni}(\text{X})\text{L}$ where L is a Horner phosphine having a (1*R*,3*R*,4*S*)-menthyl substituent (79). The optically pure (*R*)-phosphine gives rise to a

¹ The presence of ^{13}C in one of the carbonyl groups of **31** induces a new chiral center at Fe and hence the isotopomers observed in the NMR spectrum are actually diastereomers.

TABLE XVI
 ^{13}C -NMR PARAMETERS FOR $(\eta^3\text{-}(+)\text{-(1R, 5R)-PINENYL)Ni(Br)PCH}_3(\text{tert-C}_4\text{H}_9)\text{C}_6\text{H}_5$ (33)^{a,b}

Carbon	δ	$J(\text{PC})$	Δ^c	Carbon	δ	$J(\text{PC})$	Δ^c
1	49.4	4.8	0.26	10	21.3		0.06
2	128.6		0.12	11	7.8	23.8	1.16
3	81.1	20.7	0.34	12	31.1	19.7	0.16
4	29.3 ^d	2.6	0.09	13	26.7	4.7	0.30
5	40.0		0.07	14	134.4	33.3	0.84
6	29.6 ^e		0.13	15	132.9	10.8	0.35
7	46.4		0.20	16	128.1	8.7	0.07
8	39.2		0.18	17	129.8	1.9	0.04
9	26.0		0.07				

^a Mynott (50).

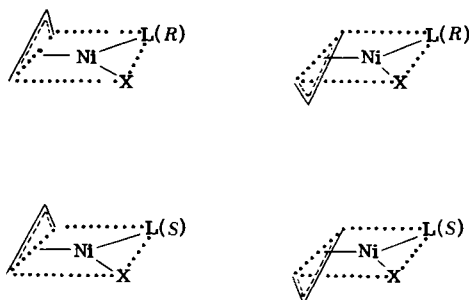
^b Benzene- d_6 , 35°C.

^c Δ = Chemical shift difference (ppm) between the diastereomers.

^d $^1J(\text{CH})$ 129 Hz.

^e $^1J(\text{CH})$ 138 Hz.

mixture of two diastereomeric complexes which differ in the orientation of the η^3 -allyl group while the epimeric (*S*)-phosphine generates two further diastereomers (33).



(33) $\text{L} = \text{PR}_1\text{R}_2(1R, 3R, 4S\text{-menthyl})$

The complexes involving menthylmethyl-*tert*-butylphosphine have been studied in most detail and will be discussed further. At 0°C the 32.4 MHz ^{31}P -NMR spectrum of the complex with the optically pure phosphine (*R* or *S*) shows the expected two signals, corresponding to the two diastereomeric complexes. However, on reduction of the temperature, each of these signals splits to give two signals of differing intensity. To obtain further information on the nature of these four species, the low-

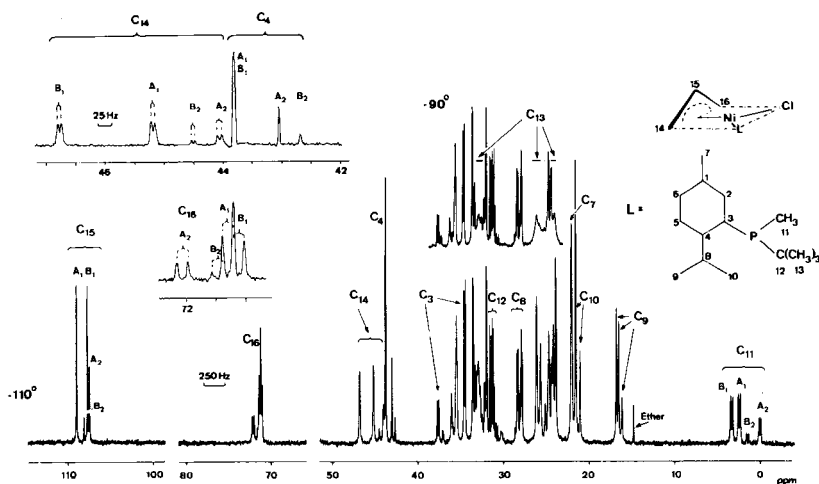
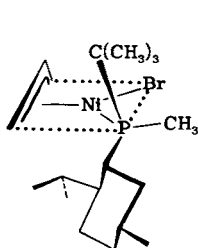
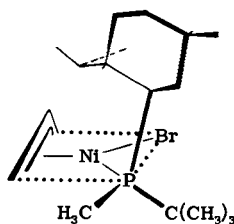


FIG. 11. ^{13}C - $\{^1\text{H}\}$ -NMR spectrum (101 MHz) of $(\eta^3\text{-C}_3\text{H}_5)\text{Ni}(\text{Cl})\text{PCH}_3(\text{tert-C}_4\text{H}_9)\text{-menthyl}$ (-110°C , toluene- d_8). At -110°C each of the diastereomers (A,B) observed at R.T. gives rise to two sets of signals (A_1, A_2 , and B_1, B_2). This is most clearly seen for C_{11} and C_{15} .

temperature ^{13}C -NMR spectra of the adduct with the (*S*)-phosphine were measured. Whereas at 0°C the ^{13}C -NMR spectra of the diastereomers are adequately resolved at 25 MHz and indicate that the conformation of the free phosphine is retained in the complex, at low temperature sufficient dispersion of the signals was achieved only by examining the complex in a superconducting system at 101 MHz. At -110°C the signals from all four components could be resolved and assigned (Fig. 11). Detailed analysis confirmed that all these species are η^3 -allyl complexes of similar geometry and the spectra are best explained as the result of restricted rotation about the nickel-phosphorus axis with the isopropyl group oriented below (a) and above (b) the plane of the complex; this is shown in **34** for one of the diastereomers. Interestingly, at -110°C the rotation of the *tert*-butyl group is slowed down sufficiently so that the three signals for the methyl groups of all four components can be observed.



(34a)



(34b)

VI

 ^{13}C DATA FOR COMPLEXED DONOR LIGANDS

The majority of the complexes discussed in the preceding sections are stabilized by donor ligands, notably phosphines or phosphites, and a short discussion of some aspects of the effect of complexation upon the ligand resonances is appropriate (see also 80).

The ^{13}C spectra of metal-complexed ligands are in general well resolved, and the signals arising from ligands such as tricyclohexylphosphine, which present problems in the PMR, can normally be assigned. In an early publication, Mann discussed the general trends of chemical shifts and coupling constants for a series of tertiary phosphines (81). We have collected representative values for free phosphines and phosphites together with their $\eta^3\text{-cyclo-C}_6\text{H}_{13}\text{Ni}(\text{Br})\text{L}$ complexes in Table XVII.

Whereas complexation has little effect on the chemical shift, the magnitudes of the $\text{P}-\text{C}_\alpha$ and $\text{P}-\text{C}_\beta$ coupling constants are often significantly altered. Analysis of the phosphorus-carbon coupling constants is complicated by a change in the sign of the coupling $^1J(\text{PC})$ from negative to positive on complexation. The changes in magnitude and sign of the coupling constants for triphenylphosphine upon complexation to molybdenum pentacarbonyl are shown in Table XVIII (82, 83).

$^2J(\text{PC})$ is usually small in the trialkylphosphine complexes. The splitting of the absorption associated with the β -carbon atoms, which is sometimes observed in the tricyclohexylphosphine and triisopropylphosphine complexes, is commonly due to diastereotopism (see Table XVII).

Bodner and Gaul have examined the ^{13}C -NMR spectra of a series of $\text{LNi}(\text{CO})_3$, $\text{LCr}(\text{CO})_3$, and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2\text{L}$ complexes (83). An analysis of the chemical shift for the *para*-phenyl resonance in phenyl-substituted ligands indicates that the electron-withdrawing character of the metal carbonyl fragment increases in the order $\text{Mn} < \text{Ni} < \text{Cr}$.

Pregosin and co-workers have shown that a detailed analysis of the trends in coupling and chemical shifts can be a valuable asset in determining the symmetry of a variety of $\text{Pd}(2+)$ and $\text{Pt}(2+)$ complexes. For example, in complexes of the type PdCl_2L_2 C_α in the ligand usually lies to lower field in the *cis* complex than in the *trans* complex while the *para* resonance in a phosphorus bonded phenyl ring is found at lower field in the *trans* complex than in the *cis* (80, 84).

Bis-Phosphine Complexes and Related Systems

In general, broad-band proton-decoupled ^{13}C -NMR spectra of un-enriched samples consist of single resonances for each type of carbon

TABLE XVII

¹³C-NMR DATA FOR *tert*-PHOSPHINES, *tert*-PHOSPHITES, AND THEIR (η^3 -cyclo-C₈H₁₅)Ni(Br)L COMPLEXES^a

Ligand	State	δC_α	$^1J(PC_\alpha)$	δC_β	$^2J(PC_\beta)$	δC_γ	$^3J(PC_\gamma)$	δC_δ	$^4J(PC_\delta)$
P(CH ₃) ₃	Free	16.5	14.0						
	Complexed	14.8	26.4						
P(C ₂ H ₅) ₃	Free ^b	18.6	11.8	9.6	12.6				
	Complexed	15.3	23.9	8.3	nd				
P(<i>n</i> -C ₄ H ₉) ₃	Free ^b	28.4	12.8	27.3	12.5	24.7	10.8	13.9	nd
	Complexed	23.8	23.0	26.8	nd	24.8	12.2	13.9	nd
P(C ₆ H ₁₁) ₃	Free	32.2	18.9	31.6	12.8	28.0	9.2	26.9	1.1
	Complexed	35.1	17.7	30.64 ^c	~0	28.09 ^c	10.0	27.0	1.2
P(C ₆ H ₅) ₃	Free	137.2	11.2	133.7	19.5	128.4	7.0	128.6	—
	Complexed	133.4	39.3	134.6	11.9	128.6	9.5	130.1	1.8
P(OC ₂ H ₅) ₃	Free	—	—	58.0	11.5	17.2	5.0		
	Complexed			61.3	1.2	16.6	6.4		
P(OC ₆ H ₅) ₃	Free	—	—	—	—	—	—	—	—
	Complexed			151.5	5.0	121.6	5.5	129.9 125.2 ^d	nd

^a From Mynott (50) and Berger (75).^b Complexes in toluene-*d*₆ at -30°C.^c Complex is chiral; C_β and C_γ are diastereotopic.^d *p*-Signal.

TABLE XVIII
VALUES OF $J(^{31}\text{P}-^{13}\text{C})$ FOR $(\text{C}_6\text{H}_5)_3\text{P}$
AND $(\text{C}_6\text{H}_5)_3\text{PMo}(\text{CO})_5^a$

	Free ligand	Complex
$^1J(\text{PC})$	$-12.51(3)^b$	$40.7(5)$
$^2J(\text{PC})$	$19.65(3)$	$10.9(5)$
$^3J(\text{PC})$	$6.80(3)$	$10.0(5)$
$^4J(\text{PC})$	$0.33(3)$	—

^a Bundgaard and Jakobsen (82); Bodner and Gaul (83).

^b An erroneous value of 21 Hz is frequently quoted.

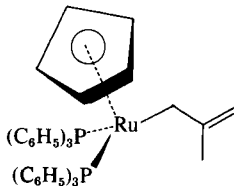
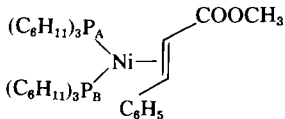
atom in the molecule. First-order splitting may arise if spin-1/2 nuclei other than ^{13}C or ^1H are present. The ^{13}C spectra may be second-order when two or more such additional nuclei are present and strongly coupled. Complexes containing two or more chemically equivalent phosphorus nuclei frequently have spectra of this type since in these systems, species (isotopomers) containing ^{13}C in the phosphorus-bonded organic groups have phosphorus nuclei that are magnetically nonequivalent. For example, in $(^{12}\text{CH}_3)_3\text{P}_\text{B}\text{M}(\text{X})_2\text{P}_\text{A}(^{12}\text{CH}_3)_2^{13}\text{CH}_3$ $^1J(\text{P}_\text{A}\text{C})$ is not equal to $^3J(\text{P}_\text{B}\text{C})$, and this and related systems frequently give rise to deceptively simple spectra. In favorable cases a complete analysis of the spectra can be made which may provide additional structural information. In practice, one must distinguish between trivial first-order spectra and second-order spectra that may be deceptively simple. Thus, a 1:1:1:1 multiplet may be a doublet of doublets from a first-order AMX system, or it could arise from an ABX system, while a 1:2:1 triplet can result from either an A_2X , an $\text{AA}'\text{X}$, or an ABX system. Examples are shown in Table XIX (50, 85).

The possibility of using ^{13}C -NMR spectroscopy to assist in assigning the geometry of bis-phosphine transition metal complexes has attracted the attention of several groups (80, 86–90). The examination of the PMR spectra of such complexes and analysis of the resulting $\text{AA}'\text{X}_n\text{X}'_n$ spectra has proved valuable (91) but has the disadvantage that it is limited to systems in which the phosphorus atom is attached to methyl, methoxy, or methylene or to related groups in which the protons couple to phosphorus but not to other protons. The condition for the observation of a 1:2:1 triplet (usually associated with trans phosphine molecules) in the proton resonance spectrum is

$$2[{}^2J(\text{PP}')] \Delta\nu_{1/2} > |J(\text{PH}) + J(\text{P}'\text{H})|^2$$

(where $\Delta\nu_{1/2}$ is the linewidth at half-height). The $\text{AA}'\text{X}$ spin system (92) encountered in ^{13}C -NMR spectra should, on the other hand, give rise to a

TABLE XIX
MULTIPLY STRUCTURE OF THE X PART OF AA'X AND RELATED SPIN SYSTEMS

Spin system ^a	Example	Comment	Multiplet structure (X part)
AMX	$(\text{CH}_3)_2\text{P}^*\text{CH}_2\text{CH}_2\text{PH}_2^b$	Trivial	Doublet of doublets
A ₂ X		Trivial	Triplet 1:2:1
AA'X	See Fig. 14	Phosphorus nuclei nonequivalent $J(\text{AX}) \neq J(\text{A}'\text{X})$	See Fig. 12; five-line multiplet, often deceptively simple
ABX	See (35)	Similar to AA'X but with small $(\delta_A - \delta_B)$ (typically ~ 0.03 ppm) due to isotope shift	Six-line multiplet similar to AA'X, but with central resonance split; see Fig. 13
ABX		$(\delta_A - \delta_B)$ larger than above; e.g., $(\delta_A - \delta_B) = 1.95$ ppm $J(\text{AB}) = 34.8$ Hz (R.T.) ^c	Six-line multiplet of which two lines may be of vanishingly low intensity

^a A, A', B, M = ³¹P, X = ¹³C.

^b King and Cloyd (85).

^c Mynott (50).

triplet when

$$8[{}^2J(PP')]\Delta\nu_{1/2} > |J(PC) + J(P'C)|^2$$

Thus, in general, smaller values for $J(PP')$ will suffice to produce a triplet in the ${}^{13}\text{C}$ spectra than in the proton spectra (88).

The most detailed analysis of these systems has been given by Nelson and co-workers (88, 89), who have simulated a series of spectra showing the variation of the ${}^{13}\text{C}$ resonance with the phosphorus–phosphorus coupling (see Fig. 12). When $J(PP')$ is large, for example in a trans complex, a 1:2:1 triplet will be observed. This becomes a five-line multiplet when ${}^2J(PP')$ is small. A doublet of doublets will be observed only if ${}^2J(PP') = 0$.

It is possible to analyze a five-line multiplet and obtain values for $J(\text{AX})$, $J(\text{A}'\text{X})$, and $J(\text{AA}')$ if account is taken of the intensities of the signals as well as their frequencies. The application to structural analysis is illustrated best by two examples, the first containing two ruthenium-bonded trimethylphosphine molecules and the second a metal-bonded chelate phosphine.

The ${}^{13}\text{C}$ -NMR spectrum of $(\eta^3\text{-}2\text{-CH}_3\text{C}_3\text{H}_4)_2\text{Ru}[\text{P}(\text{CH}_3)_3]_2$ (35) (Fig. 13) consists of only five signals, indicating that the molecule has high symmetry. The phosphine–methyl resonance (C_5) shows a splitting pattern typical for the X part of an ABX system. An analysis gives a value for

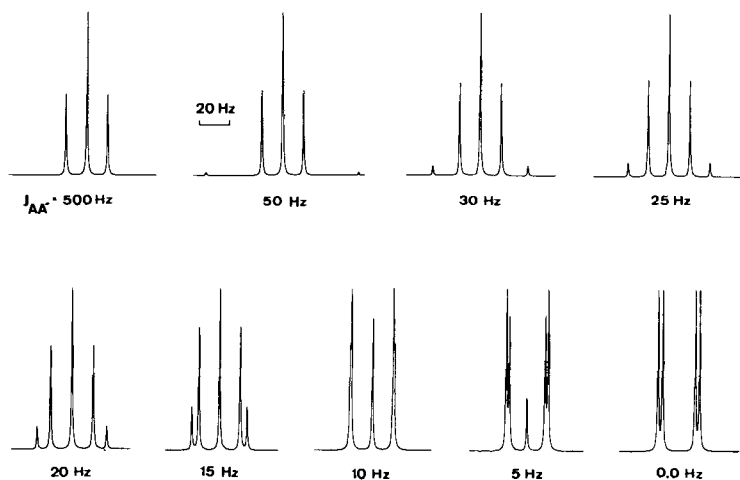


FIG. 12. Computer simulations of the X part of an $\text{AA}'\text{X}$ spin system where $J(\text{AX}) = 25\text{ Hz}$, $J(\text{A}'\text{X}) = 3\text{ Hz}$ and where $J(\text{AA}')$ is varied from 500 to 0.0 Hz. Linewidths at half-height for these simulations are 0.8 Hz [after Nelson *et al.* (88)].

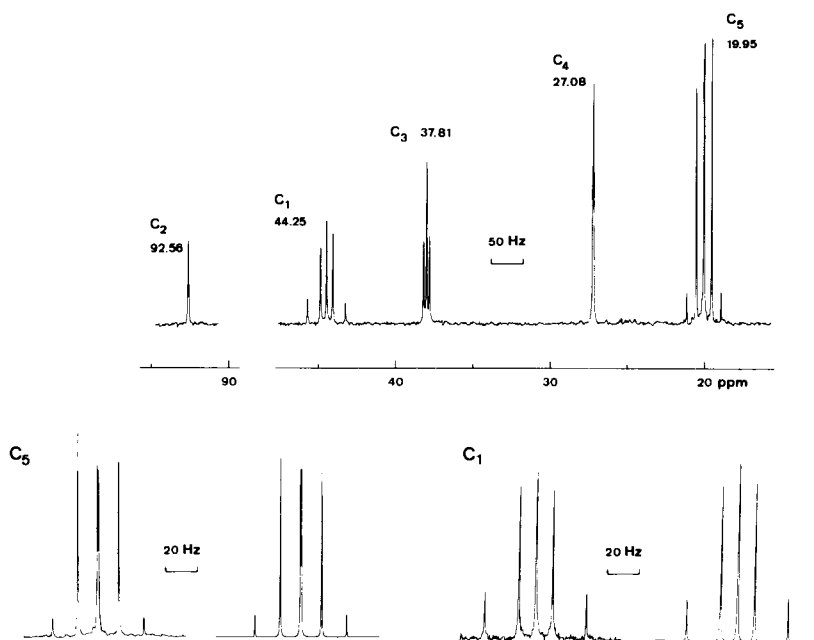
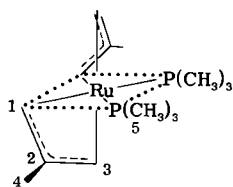


FIG. 13. ^{13}C - $\{^1\text{H}\}$ -NMR spectrum (25.2 MHz) of $(\eta^3\text{-}2\text{-CH}_3\text{C}_3\text{H}_4)_2\text{Ru}[\text{P}(\text{CH}_3)_3]_2$ (35) showing the full spectrum, expansions of the signals due to C_5 and C_1 , and their simulations (29, 50).



(35)

$^2J(\text{PP})$ of 26.2 Hz, which lies in the range expected for cis diphosphine complexes of $\text{Ru}(2+)$ (93). From the splitting of the central resonance the shift difference ($\delta\text{A}-\delta\text{B}$) in the phosphorus spectrum caused by the ^{13}C -isotopic shift is calculated to be 0.020 ppm. The multiplet at 44.3 ppm is assigned to the terminal C atoms C_1 and is apparently the X part of an $\text{AA}'\text{X}$ system. Analysis of the multiplet gives values for $|^2J(\text{PP}')|$ of 26.1 Hz and for $^2J(\text{PC})$ of ± 26.5 and ∓ 6.2 Hz. The difference in magni-

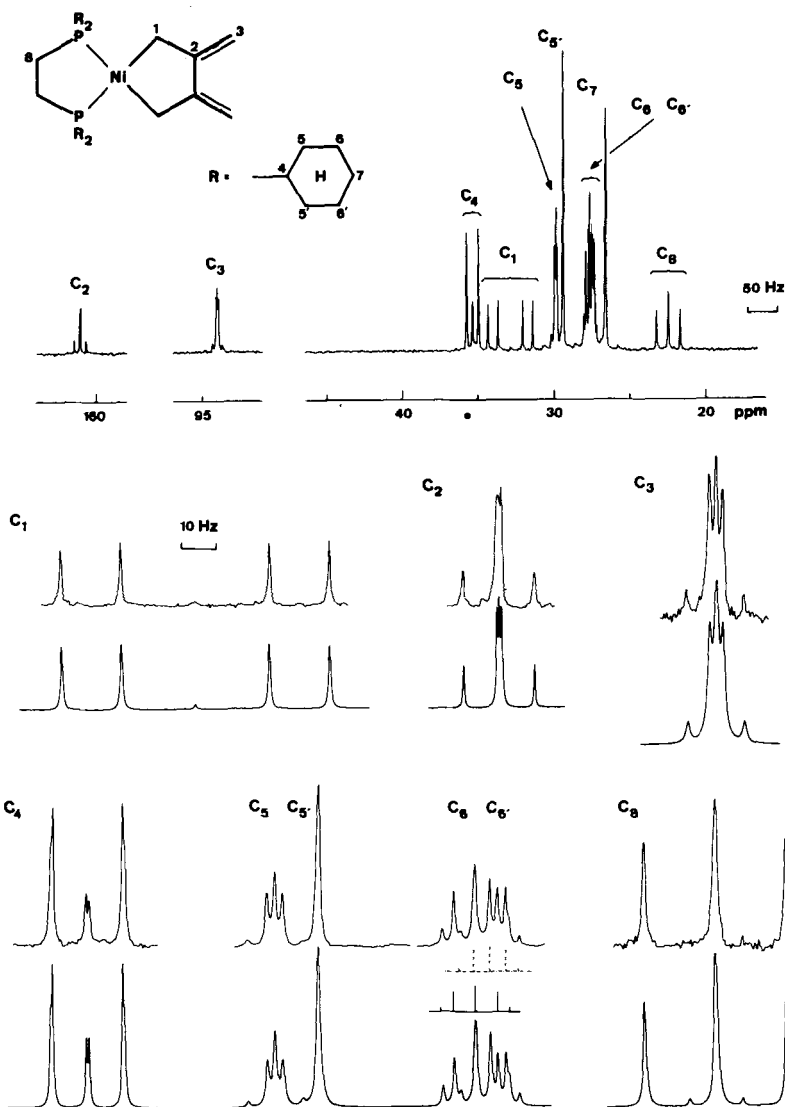


FIG. 14. $^{13}\text{C}-\{^1\text{H}\}$ -NMR spectrum (25.2 MHz) of $\text{C}_6\text{H}_6\text{NiP}(\text{C}_6\text{H}_{11})_2\text{C}_2\text{H}_4\text{PC}_6\text{H}_{11})_2$ (60°C , benzene- d_6) with expanded and simulated signals for C_1 , C_2 , C_3 , C_4 , C_5 , C_6 , and C_8 (50, 94). Assignments:

C_n	C_1	C_2	C_3	C_4	C_5	$\text{C}_{5'}$	C_6	$\text{C}_{6'}$	C_7	C_8
δC_n	33.0	161.0	94.0	35.5	30.0	29.5	27.8	27.6	26.7	22.6
$J(\text{PC})$	$\pm 56.9(1)$	$\pm 7.5(2)$	$\pm 5.4(6)$	$\pm 17.2(3)$	$\pm 5.0(9)$	— ^a	$\pm 11.8(4)$	$\pm 8.3(6)$	— ^a	— ^b
$J(\text{P'C})$	$\mp 15.7(1)$	$\mp 6.2(5)$	$\mp 1.7(6)$	$\pm 2.3(3)$	$\mp 0.7(9)$	— ^a	$\pm 0.2(4)$	$\pm 0.4(6)$	— ^a	— ^c

^a Unresolved. ^b $21.7 \approx J \geq 19.8$ Hz. ^c $17.8 \leq J \leq 19.8$ Hz.

tude and sign of these two coupling constants is consistent with an arrangement in which one of the phosphine ligands is trans to C_1 and the other cis. The intensity of the central signal can be reproduced in simulations only if a small isotope effect ($\delta A - \delta B = 0.005$ ppm) is introduced, which, however, is too small (≈ 0.2 Hz) to produce a resolvable splitting of the central resonance. The three remaining signals for C_2 , C_3 , and C_4 are apparent triplets for which a detailed analysis has not proved possible because the outer lines of the multiplets are too weak to detect. The average of the two cis couplings to C_3 is 4.8 Hz.

The second example illustrating the spectra of bisphosphine metal systems is the nickelacyclopentane complex $\text{C}_6\text{H}_8\text{NiP}(\text{C}_6\text{H}_{11})_2\text{C}_2\text{H}_4\text{P}(\text{C}_6\text{H}_{11})_2$ formed in the reaction between bis(1,5-cyclooctadiene)nickel, bis-dicyclohexylphosphinoethane, and allene (94). The ^{13}C -NMR spectrum consists of ten multiplets (three from the organic ligand and the remainder from the chelate phosphine) and contains several different types of AA'X (and ABX) multiplets (see Fig. 14). Six signals are observed for the cyclohexyl groups as a result of the chirality of the isotopomers containing ^{13}C . The β -carbon atoms (C_5 and $\text{C}_{5'}$) have a chemical shift difference of 0.48 ppm and only one of the nuclei is coupled to phosphorus. The resonances due to the γ -carbon atoms (C_6 and $\text{C}_{6'}$) are separated by 0.16 ppm. Analysis of the multiplet for C_4 gives a value of 7.1 ± 0.3 Hz for $|^2J(\text{PP}')|$ [$^1J(\text{PC}) = 17.2$ Hz, $^3J(\text{P}'\text{C}) = 2.3$ Hz], which can be used in the analysis of the remaining multiplets. The multiplet from C_1 , which appears to be a doublet of doublets, is actually part of an AA'X system with $|J(\text{PP}')|$ small relative to $J(\text{PC}) + J(\text{PC}')$; the central resonance is of very low intensity. Analysis gives values for $^2J(\text{PC})$ of ± 56.9 and ∓ 15.7 Hz and thereby excludes a pseudo-tetrahedral structure (for which two identical couplings would be expected) and indicates that the nickel atom is in an approximately square planar environment. This has been confirmed by an X-ray structure determination (94).

For C_2 the coupling constants $^3J(\text{PC})$ are approximately equal in magnitude but opposite in sign. The methylene bridge C_8 gives a multiplet of which only three lines are detected, and although a complete analysis is not possible, the sum $\Sigma ^1J(\text{PC}) + ^2J(\text{PC}')$ (39.5 Hz) as well as the range of the phosphorus-carbon couplings ($21.7 \geq J(\text{PC}) \geq 19.8$ Hz and $17.8 \leq J(\text{PC}') \leq 19.8$ Hz) can be estimated.

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